METALLIC HYDROGEN--A TWO-BODY APPROACH TO BAND THEORY AND A QUANTUM MECHANICAL TEST OF DIOPHANTINE METHODS

BY

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METALLIC HYDROGEN--A TWO-BODY APPROACH TO BAND THEORY AND A QUANTUM MECHANICAL TEST OF DIOPHANTINE METHODS

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The first part of this work demonstrates the feasibility of calculating the properties of bulk hydrogen from a periodically repeated cell of two "atoms" using biased selection. It further shows how conventional band theory can be extended to use 2-electron wave functions. Born-Oppenheimer potentials were generated for a few $\vec{k}$'s for the first three bands and for r_s = 1.23a_B, 1.48a_B, 1.97a_B, 2.96a_B and 10.84a_B ($\frac{4\pi}{3} r_s^3 \equiv$ mean volume per electron). An insulator-conductor transition was found to occur between r_s = 1.7a_B and r_s = 1.9a_B, while the solid was still molecular. A molecular-atomic transition was predicted, by extrapolation, to occur for r_s= 1.1. Finally, a significant broadening of the k-averaged Born-Oppenheimer potential takes place at r_s = 1.97a_B, where the first signs of an insulator-

conductor transition occur. (The energy is between -1.17Ry/atom and -1.15Ry/atom when the internuclear separation is between $1.25a_B$ and $2.20a_B$.) This effect is bound to have thermodynamical effects beyond those normally associated with insulator-conductor transitions.

The second part of this work details the application of Diophantine methods to the evaluation of multi-dimensional quantum-mechanical expectation values. It shows that a $\frac{1}{N}$ convergence was found for a substantial range of N, the number of multi-dimensional integration points. For the same accuracy as biased selection, Diophantine methods required one-fourth the number of points, for the remaining range of N.

INTRODUCTION

This work is most logically divided into two parts. Part I, Metallic Hydrogen--A Two-Body Approach to Band Theory, details the methods and results of a solid-state type of calculation for bulk hydrogen. Part II, A Quantum Mechanical Test of Diophantine Methods, details an exploration into the possibility of getting a convergence for general multi-dimensional integrals that is faster than the Monte Carlo convergence of $1/\sqrt{N}$. Parts I and II are self-contained: the equations and references are numbered as if the other part were not present, and the understanding of one is not required for the understanding of the other.

PART I:
METALLIC HYDROGEN--
A TWO-BODY APPROACH TO BAND THEORY

The fact that hydrogen becomes metallic under high pressure is interesting for several reasons. Firstly, theoretical calculations exist that have found the superconducting transition to be close to room temperature [1], [2]. Secondly, the interior of Jupiter contains hydrogen under high pressure ($P > 30Mb$) [3]. Thirdly, the conceptual distinction between an insulator and a conductor is clear cut. If, experimentally, hydrogen is placed under pressure with a small voltage applied to attached electrodes, either a current will flow and it is a conductor, or no current will flow and it is an insulator. If, theoretically, the first two energy bands are calculated, either they overlap and hydrogen is a conductor, or they are separated and it is an insulator at 0°K.

In this work the usual method for calculating the properties of a crystal was extended, from treating the electrons one at a time to treating them two at a time. The explicit inclusion of electron-electron distances in the wave function allowed the bulk of the correlation energy to be included. An approximate wave function for the system was constructed from 2-electron wave functions in analogy with conventional band theory. The overlapping of the first two energy bands indicated that at 0°K the molecular solid becomes a conductor for an r_s between $1.7a_B$ and $1.9a_B$ (r_s for liquid hydrogen is $\simeq 3.4a_B$, $\frac{4\pi}{3} r_s^3 = \frac{L^3}{N}$, N is the number of electrons contained in the crystal volume,

L^3). The k-averaged Born-Oppenheimer potential indicated that at 0°K the solid was still molecular for the smallest r_s used, $1.23a_B$. However, if the data are extrapolated to smaller r_s, then the molecular-atomic transition appears to occur at $r_s = 1.1a_B$. The energies found here can be used to form the partition function, from which the properties of the crystal can be calculated for temperatures less than the ionization temperature.

History

J. D. Bernal was the first to suggest that insulators would become conductors under high pressures [4]. Prior to 1974, most calculations were made assuming that the molecular-atomic and insulator-conductor transitions coincided for solid hydrogen. Atomic hydrogen has one electron per fundamental cell. Since each energy band can accomodate two electrons per fundamental cell, the valence band is only half full. This means that an atomic-hydrogen solid is necessarily a metal. Therefore, it is not clear whether assuming the two transitions coincided was a matter of belief or merely computational convenience. However, since 1974, theoretical evidence has been mounting, which this work further supports, that the solid becomes a conductor while it is still molecular [5], [6]. This makes the insulator-conductor transition a continuous function of r_s, second order, because there is no abrupt change in symmetry, from molecular to atomic, to create a discontinuity.

Wigner and Huntington were the first to calculate the properties of an atomic-hydrogen solid [4]. They used the cellular, or Wigner-Seitz, method and found an energy minimum of -1.05 Ry/atom at an r_s of $1.63a_B$. Later calculations essentially reproduced these results.

The solid hydrogen calculations fall into three general categories. There are calculations to determine the properties of the molecular solid, generally by summing over predetermined H_2-H_2 potentials [7], sometimes by using a low density expansion such as Brueckner's method [8].

These methods commonly assume the potentials to be density independent when they extrapolate the equation of state to the molecular-atomic transition density. This work casts doubts on this assumption near the molecular-atomic transition. The H-H potentials were found to depend on r_s, which makes it highly likely that the H_2-H_2 potentials will also. Furthermore, it is not clear how an H_2-H_2 potential should be defined when the molecules begin to dissociate. Some of the molecular solid calculations accurately reproduce the experimentally available equation of state ($0 \leq P \leq .025$Mb) [7].

Other calculations are on the properties of an atomic solid; Θ-function [9]; Wannier function [10]; Green's function [10], augmented plane wave [11]; exact Hartree-Fock [12], [13], [14]; perturbation theory [15], [16]; cellular [4], [17]; alternate molecular orbitals [18]; and quantum statistics [19]. Ross and McMahan [11] and McMahan [5] state that the uncertainty in the correlation energy is the outstanding problem for these methods (the energies agree to within .04 Ry/atom while the uncertainty in the correlation energy is about .13 Ry/atom). They further state that this uncertainty makes the molecular-atomic transition pressure uncertain by a factor of about two or three. This work includes the properties of a body-centered cubic atomic-hydrogen solid as a subset.

Finally, there have been a few calculations since 1974 that, like this work, use the same formalism to calculate the properties of both the atomic and the molecular forms of solid hydrogen [5], [6]. The potential and periodicity are treated somewhat more crudely here than in other methods, but this work uses much better wave functions that contain electron-electron distances explicitly.

The molecular-atomic transition pressure is usually calculated from the slope of the common tangent to the atomic-solid energy-versus-density and the molecular-solid energy-versus-density curves. This pressure is also frequently assumed to be the insulator-conductor transition pressure. This work distinguishes the molecular-atomic transition, which at 0°K did not occur for any density considered, from the insulator-conductor transition. The molecular-atomic transition takes place (at 0°K) when there is no longer a minimum in the Born-Oppenheimer potential for any nuclear-nuclear distance other than the one corresponding to a body-centered cubic atomic lattice. Also, the energy at the minimum of the k-averaged Born-Oppenheimer potential and the energy at an internuclear separation corresponding the the body-centered cubic lattice will agree at the r_s where the molecular-atomic transition occurs. The data of this work were extrapolated to find this transition. The insulator-conductor transition takes place when the bands overlap at the equilibrium separation of the nuclei.

As of 1977, Ruoff felt that there was not any convincing experimental evidence for an insulator-conductor transition in hydrogen [20]. However, a more recent experiment claims to have found one [21]. Also, there are ongoing experiments to produce an insulator-conductor transition in hydrogen [22].

The Model Hamiltonian

It is currently impossible to solve the N ($\sim 10^{23}$) particle Schrödinger equation for a general system. A standard method of dealing with this problem is to model the real system with a periodically repeated unit cell of fewer particles. In this work, two particles are placed in the unit cell and the N-particle Hamiltonian, H_N, becomes

$$H_N(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{\tilde{\ell}} H_2(\tilde{r} + \tilde{\ell}), \tag{1}$$

where the coordinates of the i^{th} electron are given by $\vec{r}_i$, $\tilde{r} = (r_{1x}, r_{1y}, r_{1z}, r_{2x}, r_{2y}, r_{2z})$ and $\tilde{\ell} \equiv (n_{1x}, n_{1y}, n_{1z}, n_{2x}, n_{2y}, n_{2z})a$. The n's are integers and "a" is the length of a side of the cubical unit cell. Since H_N is then a sum of 2-particle Hamiltonians for the different cells, the N-particle wave function will be an antisymmetrized product of 2-electron wave functions for the cells.

In the Born-Oppenheimer approximation, $H_2(\tilde{r})$ is written as

$$H_2(\tilde{r}) = -\nabla_1^2 - \frac{2}{P_{A1}} - \nabla_2^2 - \frac{2}{P_{B2}} + \frac{2}{r_{AB}} + \frac{2}{P_{12}} - \frac{2}{P_{B1}} - \frac{2}{P_{A2}} + V'(\tilde{r}),$$

where A and B refer to the nuclei, 1 and 2 refer to the electrons, and $V'(\tilde{r})$ represents that part of the potential that is not explicitly written down. The P's are the shortest distances between two particles, which can be in adjacent cells, of a given kind. Figure 1 illustrates this for a periodically repeated 2-dimensional unit cell.

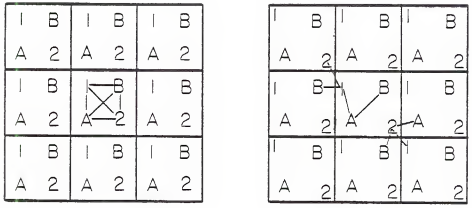

Figure 1. A periodically repeated 2-dimensional unit cell is pictured. The interparticle interactions that are considered in this work are represented by lines that connect the particles. A configuration where all interparticle distances, P's, are within the unit cell is pictured in (a). In (b) some P's are between particles in the unit cell while others are between a particle in the unit cell and a particle in an adjacent cell. In both cases, the P's are between the closest particles of a given type.

If lines were drawn to connect each particle in the unit cell with all of those particles to which it is not already connected, then these connections would represent the same interparticle interactions that $V'(\vec{r})$ does. A general group of terms would look like $-\frac{1}{r_{1A'}} + \frac{1}{r_{11'}} - \frac{1}{r_{1B'}} + \frac{1}{r_{12'}}$, where the primes are for particles not explicitly included in $H_2(\vec{r})$. The 1 in the numerator is because the remaining half of the interaction will be included in $H_2(\vec{r})$ for the cell which the primed particle occupies. Note that this group of terms is approximately zero.

In this work, $V'(\vec{r})$ is neglected. It could have been included by using an Ewald-type sum, but the desirability of including $V'(\vec{r})$ is questionable. For one thing, the imposed periodicity certainly misrepresents nature. Thus, including $V'(\vec{r})$ might actually lessen the correspondence between the model and the real system. Secondly, the real system $V'(\vec{r})$ is bound to be small due to charge neutrality and screening, especially for a conductor.

The periodicity of $H_2(\vec{r})$, i.e., $H_2(\vec{r}) = H_2(\vec{r} + \tilde{\ell})$, was used to advantage in constructing solutions to

$$H_2(\vec{r})\Phi(\vec{r}) = E\Phi(\vec{r}). \tag{2}$$

If $\Phi(\vec{r})$ is written as

$$\Phi(\vec{r}) = e^{i\tilde{k}\cdot\vec{r}}u_{\tilde{k}}(\vec{r}) \tag{3}$$

(this can always be done; e.g., let $u_{\tilde{k}}(\vec{r}) = e^{-i\tilde{k}\cdot\vec{r}}\Phi(\vec{r})$, then $e^{i\tilde{k}\cdot\vec{r}}u_{\tilde{k}}(\vec{r}) = e^{i\tilde{k}\cdot\vec{r}}e^{-i\tilde{k}\cdot\vec{r}}\Phi(\vec{r}) = \Phi(\vec{r})$), then the translational invariance of $H_2(\vec{r})$ demands that $u_{\tilde{k}}(\vec{r}) = u_{\tilde{k}}(\vec{r} + \tilde{\ell})$. That is to say that $u_{\tilde{k}}(\vec{r})$ will be periodic without approximation. However, $u_{\tilde{k}}(\vec{r})$ might only be approxi-

mately periodic for the real system. The benefits of using (3) will be discussed later.

Solving (2) for a 2-electron wave function instills a certain amount of self-consistency in the wave function, without iterating. Hartree-Fock type methods try to solve a 1-electron equation where $-\nabla_2^2 - \frac{2}{P_{B2}} - \frac{2}{P_{A2}} - \frac{2}{P_{12}} + V'(\vec{r})$ in (2) is replaced by the interaction of electron 1 with an electron charge density, the coulomb and exchange potentials. This makes it necessary to solve these equations iteratively to achieve self-consistency, since the electron charge density depends on the 1-electron wave functions that are being solved for.

If (3) is substituted into (2) and $V'(r)$ is approximated by zero, the following equation is obtained

$$\left[-\nabla_1^2 - \frac{2}{P_{A1}} - \nabla_2^2 - \frac{2}{P_{B2}} - 2i\,(\vec{k}_1 \cdot \vec{\nabla}_1 + \vec{k}_2 \cdot \vec{\nabla}_2) + \frac{2}{r_{AB}} + \frac{2}{P_{12}} - \frac{2}{P_{A2}} - \frac{2}{P_{B1}} + (\vec{k}_1 \cdot \vec{k}_1 + \vec{k}_2 \cdot \vec{k}_2 - E)\right] u_{\tilde{k}}(\vec{r}) = 0 \qquad (4)$$

This equation was solved in the Born-Oppenheimer approximation for an "H_2-molecule" in a cubical unit cell of side "a". The boundary conditions were satisfied by restricting the class of functions used to represent $u_{\tilde{k}}(\vec{r})$ (further discussion will be given later). The "molecular-axis" was along a body diagonal with its center at the cell's center. This positioning of the "molecule" allows the crystal lattice to be varied from a simple cubic molecular lattice, $r_{AB} < \frac{a}{2}\,3^{\frac{1}{2}}$, to a body-centered cubic atomic lattice, $r_{AB} = \frac{a}{2}\,3^{\frac{1}{2}}$. Two is the smallest number of "atoms" in the unit cell which will allow correlational effects to be calculated.

The Wave Function

The imposed periodicity allows an exact representation of the solutions of (2) to be written as in (3). The k-dependence of $\Phi(\tilde{r})$ makes it possible to construct a N-electron wave function from a product of Φ's with different $\tilde{k}$'s, as will be further discussed later. A 2-electron wave function allows the major portion of the correlation energy to be calculated. The relatively simple and yet accurate wave function of James and Coolidge, which explicitly includes r_{12} terms, was used as a basis for constructing $u_{\tilde{k}}(\tilde{r})$ [23]. This choice meant that 6-dimensional integrals had to be evaluated to find the expectation value of $H_2(\tilde{r})$. These integrals were evaluated using the Monte Carlo method of Appendix A. The accuracy of the wave function allowed the energy to be determined to within chemical accuracy, .01 Ry/molecule, by using less than 500,000 functional evaluations. This was accomplished by making $H\Phi/\Phi$ relatively constant, which makes the Monte Carlo error very low.

The periodic boundary conditions can be incorporated in $u_{\tilde{k}}(\tilde{r})$ as follows:

$$u_{\tilde{k}}(\tilde{r}) = \sum_{\tilde{\ell}} g(\tilde{r} + \tilde{\ell}), \tag{5}$$

where $g(\tilde{r} + \tilde{\ell})$ is a 6-dimensional generalization of

$$g(r) = \hat{g}(r) \text{ for } r < \frac{a}{2}$$

$$= \text{constant for } r \geq \frac{a}{2}.$$

This form of $g(\vec{r})$ is not mandatory, but it greatly restricts the sum in (5) to only include the unit cell. Explicit forms of $g(\vec{r})$ will be detailed shortly. Notice that in the case considered by Wigner and Seitz--an ion, with a spherically symmetric potential, and a single electron per unit cell--the above reduces to the Wigner-Seitz boundary conditions:

$$u_k(r) = \text{constant for } r \geq r_s$$

$$\left.\frac{\partial u_k}{\partial r}\right|_{r=r_s} = 0.$$

Another important similarity exists between the Wigner-Seitz method and this work. There is an implicit electron-electron correlation that is assumed for the N-electron wave function. In the Wigner-Seitz method, the assumed function is zero if any cell contains more than one electron and is otherwise unity. In this work the assumed wave function is zero if any unit cell contains more than two electrons and is otherwise unity. (Notice that this function imposes charge neutrality on the system on a cell-by-cell basis.) This function could be made more flexible by allowing it to vary between zero and one as the number of particles per unit cell varies. Lastly, the Wigner-Seitz method does not consider interactions between particles in different cells. But for one electron per unit cell, neither does this work: the distance between particles in adjacent cells is greater than $\frac{a}{2}$.

A twenty-four parameter function, modeled after James and Coolidge's function, is used to represent $u_{\tilde{k}}(\tilde{r})$:

$$u_{\tilde{k}}(\tilde{r}) = B(x_1)B(y_1)B(z_1)B(x_2)B(y_2)B(z_2)S_{A1}S_{A2}S_{B1}S_{B2}P_{JC},$$

where P_{JC} has two forms,

$$P_G = c_1 + c_2(\eta_1^2 + \eta_2^2) + c_3(\varepsilon_1 + \varepsilon_2) + 2c_4\eta_1\eta_2 + 2c_5u +$$
$$c_6(\varepsilon_1\eta_1^2 + \varepsilon_2\eta_2^2) + c_7\eta_1\eta_2(\varepsilon_1 + \varepsilon_2) + c_8(\varepsilon_1\eta_2^2 + \varepsilon_2\eta_1^2) +$$
$$c_9(\varepsilon_1^2 + \varepsilon_2^2) + 2c_{10}u^2 + 2c_{11}\eta_1\eta_2u,$$

and

$$P_E = (c_1 + c_4\varepsilon_1\varepsilon_2 + c_5u + c_8u^2)(\eta_1 - \eta_2) + c_2(\varepsilon_1^2\eta_1 - \varepsilon_2^2\eta_2) +$$
$$c_3(\varepsilon_1^2\eta_2 - \varepsilon_2^2\eta_1) + (c_6 + c_{10}u)(\varepsilon_1\eta_1 - \varepsilon_2\eta_2) +$$
$$(c_7 + c_{11}u)(\varepsilon_1\eta_2 - \varepsilon_2\eta_1) + c_9(\eta_1^3 - \eta_2^3),$$

with

$$u = 2f(P_{12})$$
$$\varepsilon_1 = f(P_{A1}) + f(P_{B1})$$
$$\eta_1 = f(P_{A1}) - f(P_{B1})$$
$$f(x) = \{-\frac{12.5}{3}[(a' - x)_+^3 - 2(a' - .2 - x)_+^3 + (a' - .4 - x)_+^3] + b\}/r_{AB},$$

and $b = \frac{12.5}{3}[a^6 - 2(a' - .2)^3 + (a' - .4)^3]$, $a' = \frac{a}{2}$. Furthermore,

$$S_{A1} = \sum_{m=12}^{20} c_m(K_m - r_{A1})_+^3 + c_{24},$$

with $K_m = (\frac{m-11}{10})\text{MIN}(\frac{a}{2}, 5)$

$$(x)_+ = x \text{ for } x \geq 0$$

$$= 0 \text{ for } x \geq 0$$

(the same c_m's and K_m's were used for all of the S's). Finally,

$$B(x) = c_{21} + c_{22}e^{-i\frac{2\pi}{a}x} + c_{23}e^{-i\frac{4\pi}{a}x}.$$

The form of f(x) insures that the P_{JC}'s satisfy the conditions of (5)--the knots are less than $\frac{a}{2}$ which drives the function to b and its derivatives to zero for $x \geq \frac{a}{2}$. The same condition is fulfilled for the S's, in the same way, except that now the constant is c_{24}. Finally, the B's are constructed so that they are explicitly periodic. The reason for two P_{JC}'s is discussed in the section on band theory. As previously mentioned, the 2-body form of $u_{\tilde{k}}(\tilde{r})$ allows the effects of 2-body correlations to be calculated. The twenty-four variational parameters, c_m's, are tabulated for the calculated wave functions in Appendix B.

The Monte Carlo Error and Finding the Eigenfunctions of Equation (4)

The biased selection method (see Appendix A) was used to estimate the expectation value of the Hamiltonian,

$$\langle E\rangle \simeq \sum E_m A_m^2 / \sum A_m^2 \ , \tag{6}$$

where $E_m = [H_2(\tilde{r}_m)\Phi(\tilde{r}_m)]/\Phi(\tilde{r}_m)$, $A_m^2 = u_k^2(\tilde{r}_m)/w(\tilde{r}_m)$, and $w(\tilde{r}_m)$ is a function that exactly compensates for the biased manner used to select $\tilde{r}_m$. Note that E_m will vary unless $u_k(\tilde{r})$ is an exact solution of (4). The estimate of the Monte Carlo error made in estimating $\langle E\rangle$ is

$$\sigma = [\sum (E_m A_m^2)^2 - 2\langle E\rangle \sum E_m A_m^4 + \langle E\rangle^2 \sum A_m^4]^{\frac{1}{2}} / \sum A_m^2 \ ,$$

where the above sums extend from m = 1 to m = M, M is the number of 6-dimensional Monte Carlo points used. Note that if $u_k(\tilde{r})$ were an eigenfunction that σ becomes $[E^2 \sum A_m^4 - 2E^2 \sum A_m^4 + E^2 \sum A_m^4]^{\frac{1}{2}} / \sum A_m^2$ which is zero. In other words, (6) would have zero Monte Carlo error. This fact was employed to find the eigenfunctions of (4) by varying the c_m's to minimize σ. After minimizing, $u_k(\tilde{r})$ is almost, but not quite, an eigenfunction. Therefore, σ will be proportional to $M^{-\frac{1}{2}}$ with a small constant of proportionality.

Equation (4) was solved by varying the twenty-four c_m's in $u_k(\tilde{r})$ to minimize σ. During the minimization, the $\langle E\rangle$ in σ had to be replaced by a constant that was less than the eigenenergy of the state being sought. Two techniques were used to vary the c_m's: (1) a routine

adapted from Nelder and Mead's simplex algorithm [24], (2) a routine that used analytically determined first derivatives, approximate second derivatives, and a matrix inversion with smoothing [25].

The first method starts with a test grid that has one more point than the number of parameters--in this case the grid has twenty-five points in a 24-dimensional space--for each of which σ is evaluated. If vectors, from the origin to the points, are used to locate the grid points, then twenty-four of the vectors must be linearly independent. The routine then generally evaluates σ for a point lying along the vector extending from the point where the largest σ was found through the "center of gravity" of the remaining points. If the σ for this trial point is less than the second highest σ (of the current twenty-five σ's), then it is kept and the highest is rejected.

The second routine heads in the direction for which σ decreases the most rapidly. Smoothing is used to make the distance moved towards the predicted minimum only a percentage of the predicted distance. This is done both to prevent the divergences frequently encountered in gradient methods and to make the expansion of σ in terms of derivatives reasonably accurate. Additionally, smoothing allows the unimportant coefficients to become zero without making the matrix singular.

A Two-Electron Approach To Band Theory

By writing the wave function as $e^{i\tilde{k}\cdot\tilde{r}}u_{\tilde{k}}(\tilde{r})$, full advantage can be taken of the similarities between this method and conventional band theory. The importance of $\tilde{k}$ here, as for the $\vec{k}$ in conventional band theory, lies in the fact that it is a good quantum number of the system and can therefore be used to label the different 2-electron states. For 1-electron wave functions and conventional band theory, the system's wave function is found by antisymmetrizing $\Psi_N = \phi_{\vec{k}_1}(1)\phi_{\vec{k}_2}(2)\phi_{\vec{k}_3}(3)\phi_{\vec{k}_4}(4) \ldots \phi_{\vec{k}_{N-1}}(N-1)\phi_{\vec{k}_N}(N)$. If it is assumed that $\varepsilon(\vec{k}_1) < \varepsilon(\vec{k}_2) < \ldots < \varepsilon(\vec{k}_N)$ then the ground state of the system will be given by antisymmetrizing $\Psi_N = \phi_{\vec{k}_1}(1)\phi_{\vec{k}_1}(2)\phi_{\vec{k}_2}(3)\phi_{\vec{k}_2}(4) \ldots \phi_{\vec{k}_{\frac{N}{2}}}(N-1)\phi_{\vec{k}_{\frac{N}{2}}}(N)$. Similar results hold for two electron wave functions: $\Psi_N = \Phi_{\vec{k}_1\vec{k}_2}(1, 2)\Phi_{\vec{k}_3\vec{k}_4}(3, 4) \ldots \Phi_{\vec{k}_{N-1}\vec{k}_N}(N-1, N)$; and assuming that $\varepsilon_{\vec{k}_1\vec{k}_1} < \varepsilon_{\vec{k}_1\vec{k}_2}$, $\varepsilon_{\vec{k}_2\vec{k}_2} < \varepsilon_{\vec{k}_2\vec{k}_3}$ etc., and that a $\Phi_{\vec{k}_n\vec{k}_n}$ can only accommodate two electrons, makes the ground state the antisymmetrization of $\Psi_{NG} = \Phi_{\vec{k}_1\vec{k}_1}(1, 2)\Phi_{\vec{k}_2\vec{k}_2}(3, 4) \ldots \Phi_{\vec{k}_{\frac{N}{2}}\vec{k}_{\frac{N}{2}}}(N-1, N)$. Finally, the properties that $\vec{k}_m$, $\varepsilon(\vec{k}_m)$, and $\phi_{\vec{k}_m}(a)$ and $\phi_{\vec{k}_m}(b)$ have in conventional band theory will also be assumed to be the properties of $\tilde{k}_m$, $\varepsilon(\tilde{k}_m)$, $\phi_{\tilde{k}_m}(a, b)$ ($\tilde{k}_m$ has the components of $\vec{k}_m$ as its first three components and as its next, and final, three components also). Thus, the eigenvalues of (4), $\varepsilon(\tilde{k}_m)$, can be used to find the energy bands. These bands are continuous functions of $\tilde{k}_m$ within each Brillouin zone,

with possible discontinuities at the zone boundaries. Remember that even though $\tilde{k}_m$ is 6-dimensional, here it consists of two 3-dimensional $\vec{k}$'s that are exactly analogous to the $\vec{k}$'s in conventional band theory. Additionally, a $\tilde{k}_m$ labels unique electron states only as long as it is contained within the first Brillouin zone. If $\tilde{k}_m$ extends beyond the first zone, then it can always be reduced back to the first zone by adding a reciprocal lattice vector to it. Therefore, $\tilde{k}_m$'s outside the first zone merely relabel a state already labeled by a $\tilde{k}_m$ within the first zone.

For $\tilde{k} = 0$, the center of the first Brillouin zone, (4) has a spectrum of eigenenergies, ε_m's. These energies can be used to generate the various energy bands, $\varepsilon_m(\tilde{k})$, as $\tilde{k}$ is varied over the first zone. It is interesting to note that if $\tilde{k}$ were varied from the center of the first zone to the center of the second Brillouin zone that $u_{\tilde{k}}(\tilde{r})$, if it were sufficiently flexible, could vary continuously from the ground state solution of (4) to either the first excited state or back to the ground state solution. This was the reason two P_{JC}'s were used. Once the ground state $u_{\tilde{k}}(\tilde{r})$ was found (using P_G), then a method was needed that would allow the first excited state to be found while guaranteeing that a poor approximation to the ground state was not found. This was accomplished by using a function, P_E, that was orthogonal to the ground state. Two states were required because the first two bands were needed to find the insulator-conductor transition.

Since P_G and P_E are the two eigenstates of lowest energy for the hydrogen molecule, they were used to generate the first two energy bands. The bands generated by P_G and P_E, ε_G and ε_E, turned out to be two approximately parallel parabolas of the form

$$\varepsilon_m(\tilde{k}) = \varepsilon_m(0) + d_m \tilde{k}\cdot\tilde{k}. \qquad (7)$$

(This form is supported by conventional band theory calculations to the desired accuracy [5], [9], [10], [15].) Apparently a band had been missed that should have roughly connected $\varepsilon_E(0)$ with $\varepsilon_G(\tilde{k}_s)$, $\tilde{k}_s \equiv \frac{\pi}{a}(1, 0, 0, 1, 0, 0)$. This is what nearly free electron band theory would lead one to predict, and there are also conventional band theory calculations that have this state. If the state existed, it could be found by directly calculating the band gap, δ , at $\tilde{k}_s$ from P_G and seeing if it was less than $\varepsilon_E(\tilde{k}_s) - \varepsilon_G(\tilde{k}_s)$. When it was calculated, δ turned out to be less than $\varepsilon_E(0) - \varepsilon_G(\tilde{k}_s)$, and thus the missing state had been found.

The band gap at $\tilde{k}_s$ was calculated by forcing $B(x_1)B(y_1)B(z_1)$ $B(x_2)B(y_2)B(z_2)$, $b(\tilde{r})$, to be $b_\pm = e^{i\tilde{k}_s\cdot\tilde{r}} \pm e^{-i\tilde{k}_s\cdot\tilde{r}}$. This creates the equivalent of the familiar forms for the wave function at the zone boundary in conventional band theory, $\cos(\frac{\pi}{a}x)\phi(x)$ and $\sin(\frac{\pi}{a}x)\phi(x)$. The $u_{\tilde{k}_s}(\tilde{r})$ with the b_+ would then be orthogonal to the $u_{\tilde{k}_s}(\tilde{r})$ with the b_-. This assured that the b_- form would give $\varepsilon_2(\tilde{k}_s)$ and not a poor approximation to $\varepsilon_1(\tilde{k}_s)$. The existence of this new energy band was further verified by varying $\tilde{k}$ slightly away from $\tilde{k}_s$ and finding energies lying on the new curve. The new energy band was taken to be an inverted parabola (i.e. $d_2 < 0$ in (7)) connecting $\varepsilon_E(0)$ and the newly found $\varepsilon_2(\tilde{k}_s) = \varepsilon_G(\tilde{k}_s) + \delta$. The first and third bands were found in a similar fashion: d_3 was chosen to connect $\varepsilon_E(0)$ with $\varepsilon_E(\tilde{k}_c)$, $\tilde{k}_c \equiv \frac{\pi}{a}(1, 1, 1, 1, 1, 1)$ and $d_3 = \dfrac{\varepsilon_E(\tilde{k}_c) - \varepsilon_E(0)}{\tilde{k}_c \cdot \tilde{k}_c}$, and d_1 was chosen to connect $\varepsilon_G(0)$ with $\varepsilon_G(\tilde{k}_c)$, $d_1 = \dfrac{\varepsilon_G(\tilde{k}_c) - \varepsilon_G(0)}{\tilde{k}_c \cdot \tilde{k}_c}$. A few additional

$\varepsilon(\tilde{k})$'s were calculated and found to fall on the predicted curves. These are the energy bands required to calculate the properties of solid hydrogen, almost.

Before continuing, a brief discussion on why $\varepsilon_3(\tilde{k})$ was found instead of $\varepsilon_2(\tilde{k})$ is in order. This problem was caused by symmetry discrepancies between P_G, and P_E and $b(\tilde{r})$. The ground state wave function, P_G, has an s-orbital type of symmetry about the box's center while P_E has a p-orbital type. Thus, for P_E to be able to give $\varepsilon_2(\tilde{k}_c)$, and not $\varepsilon_3(\tilde{k}_c)$, $b(\tilde{r})$ had to assume a form at $\tilde{k}_c$ that would make $P_E b_-(\tilde{r})$ have an s-orbital type of symmetry about the box's center, $b\pm(\tilde{r}) = e^{i\tilde{k}_c\cdot\tilde{r}} \pm e^{-i\tilde{k}_c\cdot\tilde{r}}$. Furthermore, $P_G b_-$ would have to have a p-orbital type of symmetry about the box's center. Unfortunately, $b(\tilde{r})$ was not flexible enough to have these forms. Figure 2 illustrates these symmetry conflicts.

The eigenenergies do not necessarily give the solid's energy bands. Close inspection reveals difficulties in constructing the many-body wave function from some 2-body wave functions, if Hartree-Fock theory is correct. The difficulties can be most easily visualized by trying to construct a 4-electron wave function from 2-electron wave functions. The Hartree-Fock representations of P_G and P_E are equivalent to, respectively, $\Phi_0 = \phi_0(1)\phi_0(2)$ and $\Phi_1 = \phi_0(1)\phi_1(2) - \phi_0(2)\phi_1(1)$ (where ϕ_0 and ϕ_1 are different 1-electron states). Notice that if a 4-body state is constructed from Φ_0 and Φ_1 that three particles will occupy the same 1-electron state and antisymmetrization will make this 4-body wave function identically zero. Given that Φ_0 is occupied, the next available state that a 4-body wave function can be constructed from is $\Phi_2 = \phi_1(1)\phi_1(2)$. A look at the Hartree-Fock energies for

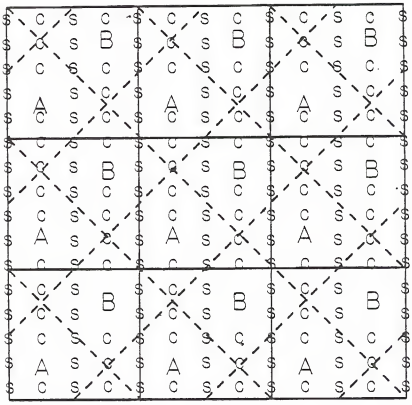

Figure 2. The nodal lines are drawn for the first excited state wave function, dashed, and for $\cos(\frac{\pi}{a}x)$, c, and $\sin(\frac{\pi}{a}x)$, s, in a periodically repeated 2-dimensional unit cell. Note that neither the c's nor the s's fall on the dashed lines. This symmetry conflict, due to the inflexibility of $b(\vec{r})$, was the reason that the eigenenergies homed in on $\varepsilon_3(\vec{k})$, instead of $\varepsilon_2(\vec{k})$. Note that the extra nodes introduced by either c or s increase the kinetic energy of the electron.

these states will show how $\varepsilon_2(0)$ and $\varepsilon_3(\tilde{k})$ must be corrected: Φ_0 has energy $\varepsilon_{00} = 2\varepsilon_0$, Φ_1 has energy $\varepsilon_{01} = \varepsilon_0 + \varepsilon_1$, and Φ_2 has energy $\varepsilon_{11} = 2\varepsilon_1$. Thus, to find the energies of the next occupiable states from the unoccupiable states given by P_E, the correct $\varepsilon_2(0)$ is given by $2\varepsilon_E(0) - \varepsilon_G(0)$ and the correct $\varepsilon_3(\tilde{k})$ is given by $2\varepsilon_E(\tilde{k}) - \varepsilon_G(\tilde{k})$. The bottom of the second band, $\varepsilon_2(\tilde{k}_s)$, did not need correcting because both electrons had been placed in an excited state. The resulting band energies are plotted in Figures 3 - 8.

As a possibly very important aside, it should be pointed out that the antisymmetrization of $\Phi_0(1, 2)\Phi_1(3, 4)$ does not give zero for general 2-electron wave functions. Therefore, if Hartree-Fock is correct, the non-zero part left after antisymmetrization must be a bad approximation to the wave function. Thus, the energy of the antisymmetrized $\Phi_0(1, 2)\Phi_1(3, 4)$ will be much larger than $\varepsilon_{00} + \varepsilon_{11}$. However, conventional band theory is known to be incorrect for certain systems [26], [27]. This breakdown could be due to the neglect of such states as $\Phi_0(1, 2)\Phi_1(3, 4)$ which might actually have energies such as $\varepsilon_{00} + \varepsilon_{01}$. At any rate, it is rather interesting that the antisymmetrizing of a product of 2-electron states to form many-electron states does not generate a "Pauli principle" as it does for 1-electron states.

Now that the energy bands have been found the k-averaged potentials can be calculated. This is accomplished by placing $\frac{2L^3}{(2\pi)^3} d\tilde{k}$ electrons in a volume, $d\tilde{k}$, in k-space. The parabolic form of the bands means that a k-sphere should be filled until it makes contact with the sides of the first Brillouin zone. Then only that part of the k-sphere inside the first zone will continue to be filled until the energy $\varepsilon_1(\tilde{k})$ is equal

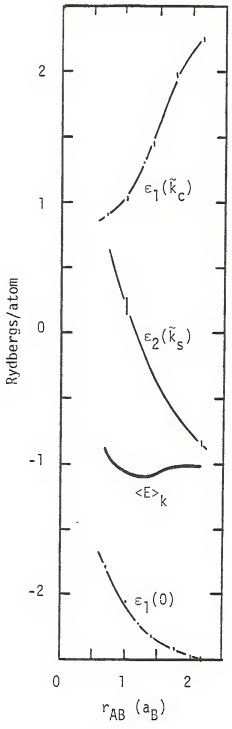

Figure 3. The top, $\varepsilon_1(\tilde{k}_c)$, and bottom, $\varepsilon_1(0)$, of the first band, the bottom, $\varepsilon_2(\tilde{k}_s)$, of the second band, and the Born-Oppenheimer potential, $\langle E \rangle_k$, versus internuclear separation are plotted, $r_s = 1.23$. The vertical lines represent the energies calculated by Monte Carlo and their σ's. Since $\varepsilon_2(\tilde{k}_s) < \varepsilon_1(\tilde{k}_c)$ for the entire range of likely r_{AB}'s, the molecular-hydrogen solid is definitely a conductor at this density. Note that even at this density the molecular solid is favored over the atomic-hydrogen solid.

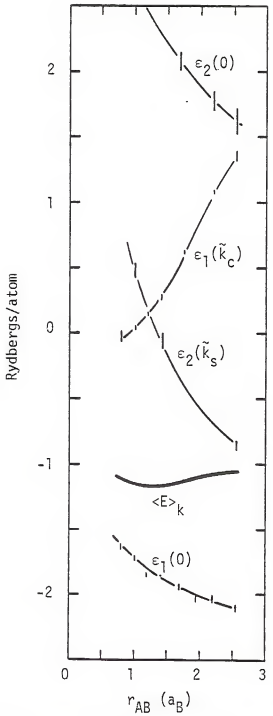

Figure 4. The tops, $\varepsilon_2(0)$ and $\varepsilon_1(\tilde{k}_c)$, and bottoms, $\varepsilon_2(\tilde{k}_s)$ and $\varepsilon_1(0)$, of the first two bands, and the Born-Oppenheimer potential, $\langle E \rangle_k$, versus internuclear separation are plotted, $r_s = 1.48$. The vertical lines represent the energies calculated by Monte Carlo and their σ's. Since $\varepsilon_2(\tilde{k}_s)$ first dips below $\varepsilon_1(\tilde{k}_c)$ for an r_{AB} that is less than the r_{AB} at the minimum of $\langle E \rangle_k$, the molecular-hydrogen solid is a conductor at this density also.

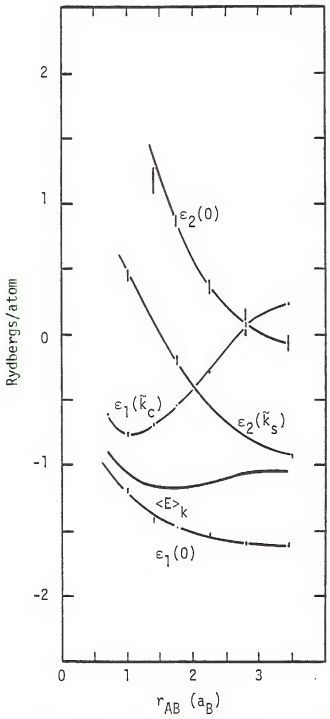

Figure 5. The tops, $\varepsilon_2(0)$ and $\varepsilon_1(\tilde{k}_c)$, and bottoms, $\varepsilon_2(\tilde{k}_s)$ and $\varepsilon_1(0)$, of the first two bands, and the Born-Oppenheimer potential, $\langle E \rangle_k$, versus r_{AB} are plotted, r_s = 1.97. The vertical lines represent the energies calculated by Monte Carlo and their σ's. Since $\varepsilon_2(\tilde{k}_s)$ does not dip below $\varepsilon_1(\tilde{k}_c)$ until r_{AB} is larger than the r_{AB} for the minimum of $\langle E \rangle_k$, the molecular-hydrogen solid will not become a conductor until the temperature is raised slightly above 0°K.

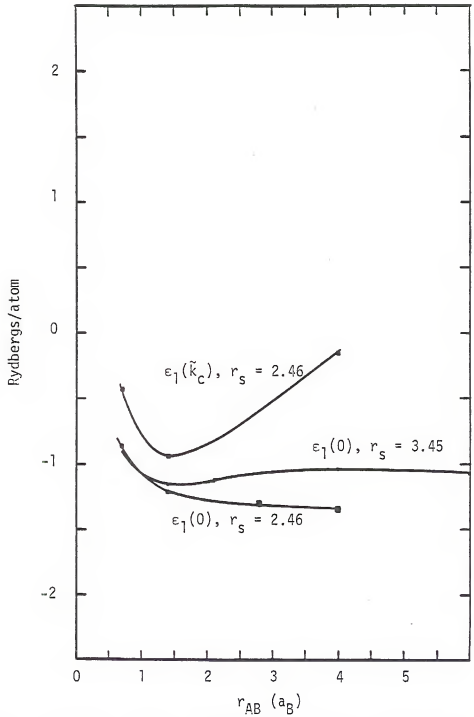

Figure 6. The top, $\varepsilon_1(\tilde{k}_c)$, and bottoms, $\varepsilon_1(0)$, of the first band for two densities, r_s = 2.46 and r_s = 3.45, versus internuclear separation are plotted. The vertical lines represent the energies calculated by Monte Carlo and their σ's.

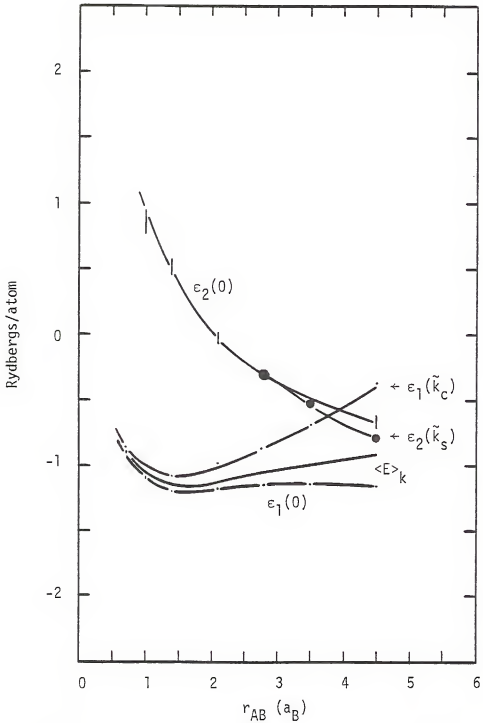

Figure 7. The tops, $\varepsilon_2(0)$ and $\varepsilon_1(\tilde{k}_c)$, and bottoms, $\varepsilon_2(\tilde{k}_s)$ and $\varepsilon_1(0)$, of the first two bands and the Born-Oppenheimer potential, $\langle E \rangle_k$, versus internuclear separation are plotted, $r_s = 2.96$. The vertical lines represent the energies calculated by Monte Carlo and their σ's. Since $\varepsilon_2(\tilde{k}_s)$ does not dip below $\varepsilon_1(\tilde{k}_c)$ until an r_{AB} well beyond the r_{AB} for the minimum of $\langle E \rangle_k$, the molecular-hydrogen solid will not be a conductor until a substantial temperature is reached.

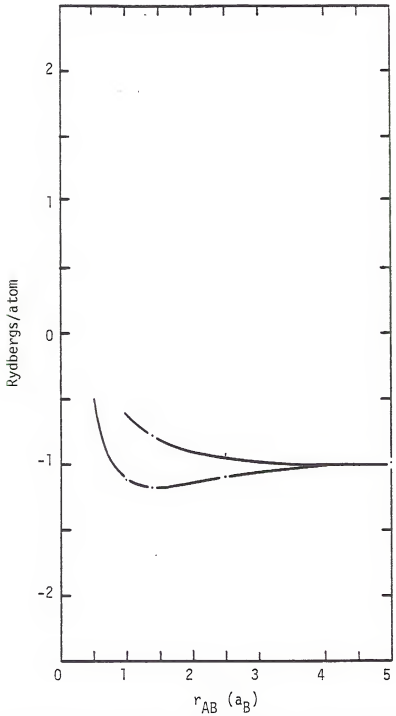

Figure 8. The first two Kolos and Wolniewicz Born-Oppenheimer potentials (solid lines) are compared with those of this work. The dots represent the energies calculated by Monte Carlo and their σ's. As expected, these potentials did not depend on k.

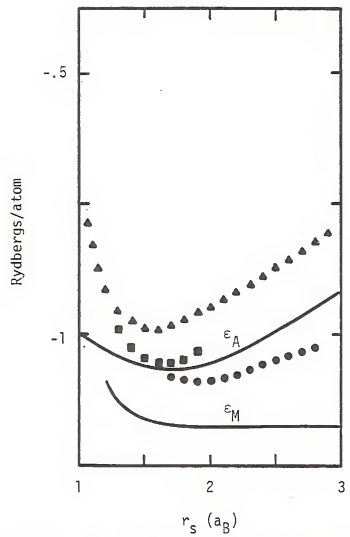

Figure 9. Comparison of this work's Born-Oppenheimer potential versus density, ε_A and ε_M, with the atomic potentials of Bellemans and De Leener [19], triangles; Wigner and Huntington [4], and Carr [16], squares; Calais [18], circles. $\varepsilon_A \equiv$ this work's atomic-solid potential for a body-centered cubic lattice. $\varepsilon_M \equiv$ this work's molecular-solid potential for a simple cubic lattice. If ε_M is extrapolated to smaller r_s, it will intersect ε_A at $r_s = 1.1a_B$; this signals the molecular-atomic transition.

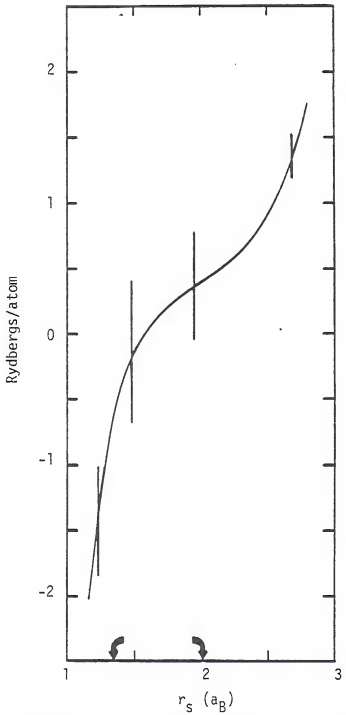

Figure 10. The band gap, $\delta = \varepsilon_2(\tilde{k}_s) - \varepsilon_1(\tilde{k}_c)$, versus density is plotted. The insulator-conductor transition occurs when $\delta = 0$. The arrows indicate the extreme limits of this transition, $r_s = 1.35$ and $r_s = 2$. The vertical lines represent the largest possible range of energies that δ could have at each density. The information for this figure came from Figures 3, 4, 5, and 7.

to $\varepsilon_2(\tilde{k}_s)$. At this time the volume inside the first zone should continue to be filled in the same manner while the volume in the second zone should be filled by occupying those parts outside of the first but inside of the second zone. (Each time a zone boundary is encountered, the above procedure would be followed.) The process is continued until a volume in k-space equal to the volume of a Brillouin zone has been filled. When the procedure is completed, all N-electrons of the solid will have been placed in states.

Results

When (4) was solved for several $\tilde{k}$'s at each r_{AB}, several r_{AB}'s at each r_s, and several r_s's for the first three energy bands, the following results were obtained. The first two Born-Oppenheimer curves of Kolos and Wolniewicz [28] were reproduced for H_2 with an r_s of $10.8a_B$, see Figure 8. The top and bottom of the first energy band were found to agree, as expected. As r_s was decreased, the bottom of the band decreased in energy while the top of the band increased, for all three bands. From $r_s = 10.8a_B$ to $r_s = 1.23a_B$, the full range of densities tested, there were no signs of a molecular-atomic transition at 0°K. However, if the data are extrapolated to smaller r_s, the transition would be predicted to occur at $r_s = 1.1$, see Figure 9. The first signs of conductivity, the overlapping of the first two bands at the equilibrium r_{AB}, appeared at $r_s = 1.97a_B$. By the time r_s was $1.23a_B$, there was no doubt that the solid was a conductor at 0°K, see Figure 10. As seen in Figure 5, a very interesting phenomenom occurs at $r_s = 1.97a_B$, where the insulator-conductor transition begins to appear. A significant broadening of the Born-Oppenheimer potential takes place, the k-averaged energy is between -1.17 Ry/atom and -1.15 Ry/atom for r_{AB} between $1.25a_B$ and $2.20a_B$. The fact that the nuclei at this, and only this, density are free to move 27% of their maximum separation possible and only change energy by 16% of the well depth, is bound to have thermodynamic consequences beyond those normally associated with insulator-conductor transitions.

Conclusion

In this work it was found that the molecular-atomic and the insulator-conductor transitions did not occur at the same density. The data indicate that the insulator-conductor transition most likely occurs between $r_s = 1.7a_B$ and $r_s = 1.9a_B$, with extreme limits of $r_s = 1.35a_B$ and $r_s = 2.0a_B$ (c.f. experiment: $r_s = 1.3a_B$ to 1.4_{ab} [21]). Extrapolation of the date indicates that the molecular-atomic transition occurs at $r_s = 1.1a_B$. Finally, the distinct widening of the minimum of the k-averaged Born-Oppenheimer potential at $r_s = 1.97$ is bound to have thermodynamical consequences beyond those normally associated with insulator-conductor transitions.

In this work it was also successfully demonstrated that 2-electron wave functions could be used in band theory. This work also opened the door to further possibilities. The Born-Oppenheimer potentials can be used to determine the nuclear motion and quantum solid effects. The data can be used to find the Slater sum, from which the thermodynamics of bulk hydrogen can be determined. The kind of "atoms" in the unit cell can be altered so that new systems could be explored. Even the number of particles per unit cell could be increased.

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PART II:
A QUANTUM MECHANICAL TEST OF DIOPHANTINE METHODS

The wave functions in Part I were calculated by varying the twenty-four parameters to minimize the Monte Carlo error in estimating the energy, using roughly 1,000 functional evaluations. However, to reduce the Monte Carlo error in estimating the energy for the final set of twenty-four parameters, 500,000 functional evaluations were required. Thus, 499,000 functional evaluations are used not in improving the wave function but only in reducing the Monte Carlo error of the energy estimate to acceptable levels. Obviously, it would be a big help if the required number of functional evaluations could be reduced. In this part of the ~~thesis~~ dissertation, a method is presented which can decrease the required number of functional evaluations by a factor of four.

In particular, a numerical experiment was conducted to compare the biased selection method [1] of evaluating the expectation value of the Hamiltonian for a dihydrogen molecule -- using the 11-term James-and-Coolidge wave function, Ψ_{JC}, [2] -- with a blend of the biased selection and Haselgrove's method [3]. In its essence, the blend amounted to using Haselgrove's method of generating numbers in place of the random number generator used by the biased selection method (the latter method is a Monte Carlo scheme). The results were mixed. The "blend" gave an error proportional to either $\frac{1}{N}$ or $\frac{1}{\sqrt{N}}$ depending on whether N was, respectively, less than or greater than 60,000

(N ≡ the number of functional evaluations). The "blend" also gave an error that went from being larger than the biased selection error (for N < 10,000) to being only half as large for N > 60,000. These numbers should be compared with the 10,000 points used in finding an optimum set of Haselgrove's parameters. It is reasonable to expect that if 100,000 points were used in the optimization of Haselgrove's parameters that the above results would be found with 60,000 replaced by 600,000. At any rate, a faster rate of convergence than $\frac{1}{\sqrt{N}}$ was found for a large range of accessible N.

Haselgrove's Method

Haselgrove's method was investigated to see if it could be used to give a more rapid rate of convergence in estimating the multi-dimensional integrals encountered in quantum mechanics than the Monte Carlo methods in current use. His method promises an N^{-i} (with $i \geq 1$) convergence for integrands which are fourier expandable and whose derivatives satisfy certain continuity conditions. The method uses

$$S_N = f(\vec{o}) + 2 \sum_{m=1}^{N} c_m f(|2Lm\alpha_1|, \ldots, |2Lm\alpha_K|) \qquad (1)$$

to estimate the integral $(2L)^{-K} \int \ldots \int f(\vec{x}) d\vec{x}$, call it I, when $f(\vec{x})$ is an even function (K ≡ the dimensionality, $f(\vec{x}) \equiv f(x_1, \ldots, x_K)$, $d\vec{x} \equiv dx_1 \ldots dx_K$). The c_m's (which are functions of N, m, and i) determine the rate of convergence, the value of i . The α_i's are irrational numbers, which must be found and which admit no solutions to $1 + \sum_{i=1}^{K} M_i \alpha_i = 0$ when the M_i's are integers.

For i equal to two , the integrand $W(\vec{x}) \equiv \prod_{i=1}^{K} (1 - |x_i|)^2$, where $2^{-K} \int_{-1}^{1} \ldots \int_{-1}^{1} W(\vec{x}) d\vec{x} = 3^{-K}$, gives the worst possible error, ε_w, (to within a multiplicative constant that depends on the specific integral being evaluated but not on N) of all the integrands satisfying Haselgrove's conditions. The key to finding the $\vec{\alpha}_i$'s lies in minimizing ε_w. This was done by selecting K random numbers (between 0 and 1) and varying them by a simplex method [4] to minimize ε_w. Tables I and II give some $\vec{\alpha}$'s and corresponding ε_w's as functions of N.

Table I. This table contains the $\vec{\alpha}_{KM}$ found by minimizing ε_w over K-dimensions, using either my method (second subscript M) of finding $\{2m\alpha_i\}$ or Haselgrove's method (second subscript H).

$\vec{\alpha}$ optimized over 1,000 points

α_{5M}

.45260537885008
.47561868232093
.57787664217299
.49493808300031
.21929292303371

$\vec{\alpha}$ optimized over 10,000 points

α_{5M}

.45241479419455
.47565271662758
.5782437781132
.49509111688911
.21929571968924

α_{5H}

.957286852634
.86730302040274
.097247969465186
.31301711424498
.48486758446139

$\vec{\alpha}$ optimized over 10,000 points

α_{6M}

.43657287149021
.59181442054365
.050243216161086
.84377789758502
.38121353509683
.78500128467888

α_{8M}

.73778770979932
.083137623602196
.84742517966315
.88984806744176
.80256318005657
.27985939980508
.67436009334498
.5303179412788

Table II. This table gives the absolute value of the difference, multiplied by 10 , between W and Haselgrove's estimate of W, using my method of finding $\{2m\alpha_i\}$ (ε_{WM}) and Haselgrove's (ε_{WH}).

N	ε_{WH}	ε_{WM}
($\vec{\alpha}_{5M}$ optimized over 1,000 points)		
1000	9774	5570
3000	2338	1876
7000	887	596
15000	237	249
31000	125	118
59000	68	47
($\vec{\alpha}_{5M}$ optimized over 10,000 points)		
1000	7818	7404
3000	3173	2225
7000	1289	541
15000	299	191
31000	112	72
59000	42	35
($\vec{\alpha}_{5H}$ optimized over 10,000 points)		
1000	5980	5434
3000	1326	1179
7000	405	447
15000	143	223
31000	63	95
59000	38	43
($\vec{\alpha}$ from Haselgrove's paper)		
1000	5933	5716
3000	1592	1808
7000	455	1086
15000	282	732
31000	178	462
59000	114	241

It can be seen that ε_{WH} and ε_{WM} have been substantially lowered from those given by Haselgrove's original $\vec{\alpha}$. Also note that ε_{WH} and ε_{WM} differ by less as N is increased, regardless of which method was used to find $\{2m\alpha_i\}$. Furthermore, the ε_W's for $\vec{\alpha}_{5H}$ and $\vec{\alpha}_{5M}$, optimized over the same number of points, differ by less as N is increased.

If c_m is equal to $\frac{N+1 - |m|}{(N+1)}$ or $\frac{1}{2N+1}$ then an i equal to 2 or 1 should be found. The main reason an i equal to 1, instead of 2, might be used is because Haselgrove's method places less stringent demands on the integrand for smaller i's. In the experiment, both i's were found to give the same convergence.

Eventually, $2m\alpha_i$ will fall outside the integration region as m is increased. Two distinct methods were used to reduce $2m\alpha_i$ to the integration region: Haselgrove's used $2[\![\frac{m\alpha_i}{2}]\!]$ for each x_i ($[\![x]\!]$ is the signed distance to the nearest integer, e.g., $[\![1.9]\!] = -.1$ and $[\![2.1]\!] = +.1$), my way used the periodic equivalent of $2m\alpha_i$ lying within the interval from -1 to +1. (In either case, denote this reduced number by $\{2m\alpha_i\}$.) The $\vec{\alpha}$ that is found by varying an initial $\vec{\alpha}$ to minimize ε_w, will depend on the method used to find $\{2m\alpha_i\}$. If one method is used to find $\{2m\alpha_i\}$ for the minimization and the other method is used to find $\{2m\alpha_i\}$ in estimating I, then reasonable, although not optimal results, will be found. In the experiment, both methods gave equivalent error estimates.

The α_i's used in the experiment had a 14-digit computer representation. Since the α_i's are represented by a computer, they are not irrational. This fact will be a problem when N is roughly 10^7 [5].

Haselgrove's Method Used by Itself

Haselgrove's method was used to estimate the known values of some definite integrals. His $\vec{\alpha}$ was used to estimate the value of the 5-dimensional integral $\int_0^1 \cdots \int_0^1 e^{-x_1x_2x_3x_4x_5} dx_1 dx_2 dx_3 dx_4 dx_5$, and his results were reproduced exactly.

The method was then tested on a problem that required a change of variables. The expectation value of the Hamiltonian for a helium atom -- using $\Psi = e^{-zs}$, $z = \frac{27}{16}$, $s \equiv r_1 + r_2$, $r_i \equiv$ nuclear-electron separation -- was estimated. This expectation value can be determined by evaluating

$$L \equiv 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt (8su - s^2 + t^2) e^{-2zs},$$

$$M \equiv 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt\, e^{-zs} \{u(s^2 - t^2)[\Psi_{ss} + \frac{2}{u}] + 4us\Psi_s\}, \tag{2}$$

and

$$\text{Norm} \equiv 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt\, u(s^2 - t^2) e^{-2zs}$$

where $\Psi_s \equiv \frac{\partial \Psi}{\partial s}$ [6]. Haselgrove's method, since it is designed to sample the 3-dimensional space uniformly, will sample the important region of the integrand with a very low probability. In order to increase the probability of sampling the important regions, a change of variables, which amounts to importance sampling [5], can be employed

$$s' = -\&n(1 - s), \quad t' = \frac{t}{u}, \quad u' = \frac{u}{s}.$$

These transformations alter Eqs. (2) to

$$L = 2\pi^2 \int_0^1 ds \int_0^1 dt \int_0^1 du \{u(1-s)^{2z-1}[8u - 1 + u^2t^2] \&n^4(1-s)\}$$

$$M = 2\pi^2 z^2 \int_0^1 ds\,dt\,du \{(1-s)^{2z-1} u^2 [1 - u^2t^2 + \frac{4}{z\&n(1-s)}] \&n^5(1-s)\} \quad (3)$$

$$\text{Norm} = 2\pi^2 \int_0^1 ds\,dt\,du \{u^2(1-x)^{2z-1}[1 - u^2t^2] \&n^5(1-s)\}.$$

In Eqs. (2) and (3), M, L, and Norm are the expectation of ∇^2, the potential, and 1, respectively. Table III gives some results.

This problem has an interesting feature: the variable transformation introduces singularities into the first derivative of the integrand. Even with this violation of Haselgrove's conditions, the results in Table III seem to give a better convergence than $\frac{1}{\sqrt{N}}$.

The results with helium were good enough to warrant moving on to a problem which is more difficult--the evaluation of the expectation value of the Hamiltonian for the dihydrogen molecule, using Ψ_{JC}. First, Haselgrove's method alone was used, with the results given in Table IV. The lack of any signs of a $\frac{1}{N^2}$, or even a $\frac{1}{N}$, convergence was not unexpected for the N used (the problem, in helium, of sampling the important region frequently enough is made more severe here due to the increased dimensionality). Next, Haselgrove's and the biased selection methods were combined with the hope of gaining the advantages of both. Biased selection would be a way of sampling the important regions more frequently, taking the place of the importance sampling used for helium. By replacing the random number generator with Haselgrove's method of generating points in a multi-dimensional space, we hoped to gain the advantages of sampling the important

Table III. Energy bounds, $\int \Psi H \Psi d\vec{r}_1 d\vec{r}_2 / \int \Psi^2 d\vec{r}_1 d\vec{r}_2$, for a helium atom were calculated using Haselgrove's $\vec{\alpha}$ and two different methods.

N	Haselgrove's Method	$4E\varepsilon_W$	My Method	$4E\varepsilon_W$
1000	-5.697346	.002644	-5.700216	.003694
3000	5200	611	5.695513	570
5000	026	319	516	228
7000	189	182	350	137
9000	358	114	354	91
11000	338	68	29	68
13000	305	68	15	46
15000	278	68	23	46
17000	285	46	27	46
19000	298	46	15	23

For comparison the exact value of the integrand, which is not the exact ground state energy, is -5.695313. All answers are in Rydbergs. The error estimates, $4E\varepsilon_W$, were calculated by assuming that the error in each integral in Eq. (3) was ε_W, and then by taking small ε_W limit.

Table IV. This table gives estimates of the expectation value of the hydrogen molecule, using James and Coolidge's 11-parameter wavefunction and Haselgrove's method without the aid of biased selection (all energies are in Rydbergs and the correct answer is 02.34609).

N	$\langle E \rangle_H$	$\langle E \rangle_H$
1000	-2.31939	-2.49532
3000	-2.22855	-2.22018
7000	-2.22166	-2.23877
15000	-2.23085	-2.24075
31000	-2.23844	-2.25364
59000	-2.25539	-2.23981

The second column gives the results when Haselgrove's method was used to find $\{2m\alpha_i\}$. The third column gives the results when my method was used to find $\{2m\alpha_i\}$. Because it can be difficult to sample the important regions of a 6-dimensional integrand, the poor results were not unexpected. Compare these results with the results of Table V where the help of biased selection was employed. The α_{8M} from Table I was used.

regions with more uniformity [5], [7]. In other words, an error estimate which was proportional to $\frac{1}{N}$ rather than $\frac{1}{\sqrt{N}}$ seemed possible.

Haselgrove's Method Used in Combination with Biased Selection

The evaluation of $E = \int \Psi_{JC} H \Psi_{JC} d\vec{x} / \int \Psi_{JC}^2 d\vec{x}$ was carried out over an integration region which was a box of length $L_x = 20a_B$, ($L_y = L_z = 22a_B$, $a_B \equiv$ Bohr radius) in the x (y, z) direction. This box is large enough to insure the desired accuracy. The two nuclei are fixed on the z-axis with the point halfway between them coincident with the center of the box.

If the biased selection method were going to be used to estimate E, then the following could be done. Select the coordinates of the first electron in four ways and those of the second in five ways (four ways being the same as for the first electron). The estimator for E would be

$$B_N = \frac{1}{N} \sum_{i=1}^{N} f(\vec{x}_i)/\overline{w}(\vec{x}_i), \tag{4}$$

where the relative probability of selecting a 6-dimensional $\vec{x}_i$, $\overline{w}(\vec{x}_i)$, exactly corrects for the non-uniform selection of the $\vec{x}_i$'s. If each of the twenty ways (four ways for the first electron times five ways for the second) of selecting an $\vec{x}_i$ is used with equal probability then

$$\overline{w}(\vec{x}_{1i}, \vec{x}_{2i}) = \frac{1}{4}[w_1(\vec{x}_{1i}) + w_2(\vec{x}_{1i}) + w_3(\vec{x}_{1i}) + w_4(\vec{x}_{1i})] \times \frac{1}{5}[w_1(\vec{x}_{2i}) + w_2(\vec{x}_{2i}) + w_3(\vec{x}_{2i}) + w_4(\vec{x}_{2i}) + w_5(\vec{x}_{2i})].$$

These w_1's, etc., are determined by the methods used to select the

electrons' coordinates:

$$x = R_1 L_x,\ y = R_2 L_y,\ z = R_3 L_z$$

$$w_1(\vec{x}_1) = 1$$

($R_i \equiv$ random number uniformly selected between 0 and 1, a total of six R_i's are needed for each $\vec{x}_i$ in Eq. (4))

$$r_c = \sqrt{R_1} M_c,\ \mu = 2R_2 - 1,\ \phi = 2\pi R_3$$

$$w_2(\vec{x}_1) = V/(2\pi M_c^2 r_c)$$

($r_c \equiv$ the electron's distance from the center, $\mu \equiv$ the cosine of the angle between r_c and the y-axis, $\phi \equiv$ the angle between the projection of r_c in the x-y plane and the x-axis, $V = L_x L_y L_z$, M_c is a constant)

$$\mu_a = 2R_2 - 1,\ \phi_a = 2\pi R_3$$

r_{ai} is selected by requiring

$$\int_0^{r_{ai}} g(y)dy \Big/ \int_0^{8} g(y)dy = R_1$$

$$w_3(\vec{x}_i) = \frac{Vg(r_{Ai})}{4\pi r_{Ai}^2 \int_0^{8} g(y)dy}$$

$$w_4(\vec{x}_i) = \frac{Vg(r_{Bi})}{4\pi r_{Bi}^2 \int_0^{8} g(y)dy}$$

(a = A or B, i = 1 or 2, $r_{ai} \equiv$ the distance between nucleus a and electron i)

$$r_E = \sqrt{R_4}M_E,\ \mu = 2R_5 - 1,\ \phi = 2\pi R_6$$

$$w_5(\vec{x}_2) = V/(2\pi M_E^2 R_E)$$

($r_E \equiv$ the electron-electron distance, $M_E \equiv$ a constant). The function $g(r)$ was created by evaluating r^2e^{-2r} at 64 points and connecting these values with line segments.

The estimator that is used to estimate E_0 is

$$c_N \equiv \frac{\sum_{i=1}^{20}\sum_{m=1}^{N} \Psi_{JC}(\vec{x}_{im})H\Psi_{JC}(\vec{x}_{im})/\overline{w}_i(\vec{x}_m)}{\sum_{i=1}^{20}\sum_{m=1}^{N} \Psi_{JC}^2(\vec{x}_{im})/\overline{w}_i(\vec{x}_m)}, \tag{5}$$

where $\overline{w}(\vec{x}) \equiv \frac{1}{4}[w_1(\vec{r}_1) + w_2(\vec{r}_1) + w_3(\vec{r}_1) + w_4(\vec{r}_1)] \times$

$$\frac{1}{5}[w_1(\vec{r}_2) + w_2(\vec{r}_2) + w_3(\vec{r}_2) + w_4(\vec{r}_2) + w_5(\vec{r}_2)]$$

($\vec{r}_i \equiv$ electron's coordinates, $\vec{x}$ represents an $\vec{r}_1$, $\vec{r}_2$ pair). The i in Eq. (5) signifies which of the twenty ways (four ways for the first electron times five ways for the second) is to be used to generate $\vec{x}_{im}$ from $\{2m\vec{\alpha}\}$, for a given m. (This same $\{2m\vec{\alpha}\}$ is used to generate a total of twenty $\vec{x}_{im}$'s.) This procedure is used (instead of using an 8-dimensional $\vec{\alpha}$ and using the two extra α_i's to randomly select which of the four (five) ways would be used to select the first (second) electron's coordinates, as can be done in the usual biased selection) to insure that $\vec{x}_{im}$ will be close to $\vec{x}_{in}$ if $\{2m\vec{\alpha}\}$ is close to $\{2n\vec{\alpha}\}$. Note that for c_N to be fairly compared with a Monte Carlo estimate that the Monte Carlo estimate would have to use 20N functional evaluations.

Table V. Energy bounds (in Rydbergs) for an H_2 molecule calculated using the 11-term James-and-Coolidge wave function and using α_{8M} from Table I to generate the "random numbers" that were used to determine the electron positions.

N	Energy Bound	$4E\varepsilon_W$
1000	-2.34684	.006982
3000	560	1736
7000	585	619
15000	596	241
31000	601	105
57000	607	57

The blend of Haselgrove's and the biased selection method was used. The exact answer, to six digits, for the given wave function, is -2.34609 Ryd [2].

Further Tests of the Blend of HaselGrove's and the Biased Selection Methods

One must be careful to insure that the method of generating the $\vec{x}_i$'s is not creating correlations between the $\vec{x}_i$'s. A commonly used random number generator, furnished by IBM with their FORTRAN compiler, was found to have this defect [8]; the random number generator used for the calculation herein did not. Therefore, Haselgrove's method was used to calculate the nuclear-electron and, especially, the electron-electron correlation functions. These functions were then compared with the correlation functions generated by using biased selection. The functions found by the two methods agreed, indicating that the configurations generated from $\vec{\alpha}$ did not have any correlations that were not due to particle-particle interactions. The correlation functions can be compared in Figures 1 and 2.

Unwanted correlations were also tested for by seeing if the configurations generated by using Haselgrove's scheme, without the help of biased selection, were uniformly distributed throughout the volume. This was done by dividing the 6-dimensional integration volume into 729 equal-volume hyper-cubes--i.e., three equally spaced divisions were made in each dimension--and noting the distribution of points within them. Figure 3 illustrates that the number of points per hyper-cube was normally distributed and that this distribution has less deviation than uniformly and randomly distributed points have, as expected.

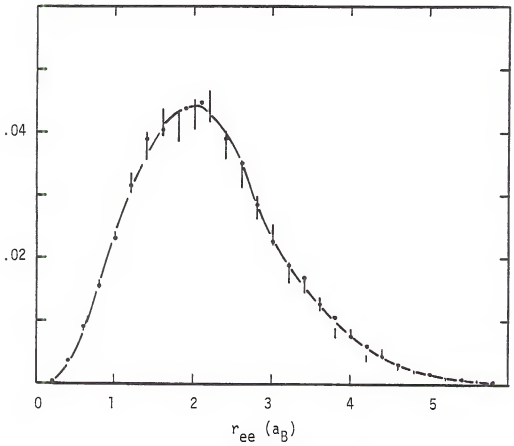

Figure 1. Comparison of the biased selection method (|) and the blend of biased selection and Haselgrove's method (•) for calculating the electron-electron correlation function. The biased selection method used 40,000 points and the 'blend' used the equivalent of 200,000 Monte Carlo points. The excellent agreement demonstrates that the points generated by the 'blend' did not introduce any non-physical electron-electron correlations.

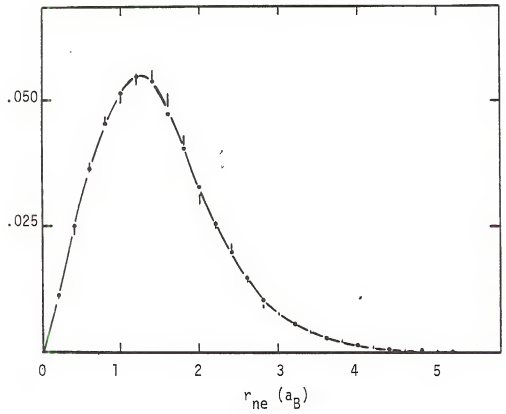

Figure 2. Comparison of the biased selection method (|) and the blend of biased selection and Haselgrove's method (·) for calculating the nuclear-electron correlation function. The biased selection method used 40,000 points and the 'blend' used the equivalent of 200,000 Monte Carlo points. The excellent agreement demonstrates that the points generated by the 'blend' did not introduce any non-physical nuclear-electron correlations.

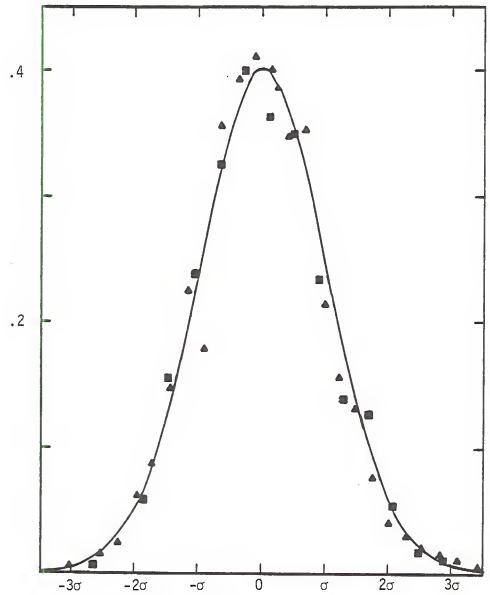

Figure 3. N points were placed in a 6-dimensional volume that was divided into 729 equal cells, using Haselgrove's method. The number of points falling in each cell was counted, and the mean and standard deviation of these 729 numbers were calculated. The fraction of cells containing a number of points which was a given number of standard deviations away from the mean was plotted. The squares are the results of a 10,000 point run: mean = 13.7, σ = 2.53. The triangles are the results of a 20,000 point run: mean = 27.4, σ = 3.73. A normal curve is drawn for comparison. Also for comparison, a purely random set of 10,000 (20,000) points would be expected to have a mean of 13.7 (27.4) and σ of 3.70 (5.23).

Monte Carlo Estimation of the Error

Since ε_w, at best, can only determine an error estimate for Eqs. (1), (4), and (5) to within an undetermined multiplicative constant, which is independent of N, some trial-and-error searching would be required to find this constant. But there is a very real danger in this type of an approach. If the constant, B, is large enough to ensure that $\frac{B}{N}$ is larger than the difference between c_N and the correct answer for some N_B, then the error might be overestimated for smaller N and, at the same time, be underestimated for larger N. In the case of estimating E_0, the 5-decimal place accuracy quoted by James and Coolidge was approximately achieved for N = 59,000. Therefore, the B that would be correct here could not be tested by increasing N. In order to obtain a reliable error estimate, a Monte Carlo procedure was used.

In place of Eq. (1), the following estimator

$$S_N(\vec{R}_i) \equiv \sum_{m=1}^{N} c_m f(|2m\alpha_1 + R_{1i}|, \ldots, |2m\alpha_K + R_{Ki}|)$$

can be used without violating any of Haselgrove's conditions ($\vec{R}_i$ is a set of K random numbers selected uniformly from the interval between 0 and 1). By selecting M $\vec{R}_i$'s and estimate can be made of the average and the standard deviation of the distribution of $S_N(\vec{R}_i)$'s. The standard deviation can be used as an error estimate for any given S_N,

$$\varepsilon = \left[\frac{1}{M}\sum_{i=1}^{M}(S_N(\vec{R}_i) - \frac{1}{M}\sum_{j=1}^{M} S_N(\vec{R}_j))^2\right]^{\frac{1}{2}}.$$

An estimate of the error in estimating ε is

$$\delta = \sqrt{\frac{2}{M}}\,\varepsilon.$$

To prevent the overhead in finding ε and δ from going to waste, the following refined estimates of I and its error can be used:

$$I \simeq \frac{1}{M_1}\sum_{i=1}^{M} S_N(\vec{R}_i)$$

with the error in the above estimate given by

$$\varepsilon_I = \frac{\varepsilon}{\sqrt{M}}.$$

Figure 4 displays some results.

It is interesting to note that for N less than or on the order of 10,000 --the number of configurations used to optimize $\vec{\alpha}$ -- that the convergence appears to be $\frac{1}{N}$, but for N very much larger than 10,000 the convergence becomes $\frac{1}{\sqrt{N}}$. This suggests the possibility of extending the $\frac{1}{N}$ convergence to larger N by increasing the number of points used to optimize $\vec{\alpha}$.

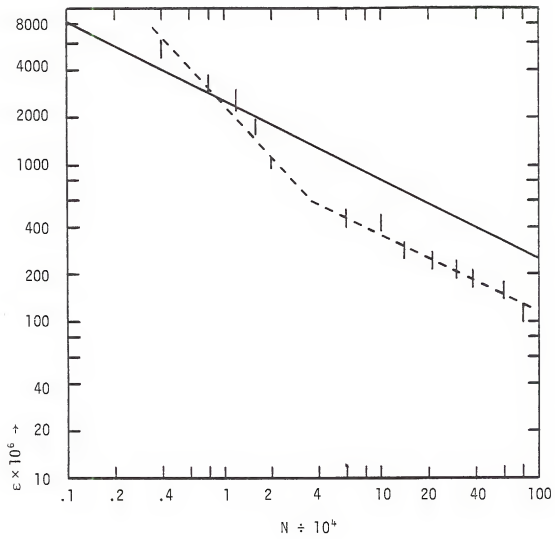

Figure 4. Comparison of the error using biased selection (straight line prediction from 40,000 points) and the error using the blend of biased selection and Haselgrove's method (vertical lines). The size of the vertical lines represents the possible error, δ, in estimating the error, ε.

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CONCLUSIONS OF DISSERTATION

The calculations of Part I required an enormous amount of computer time, roughly 1200 hours of Amdahl 470 cpu time. While experience would allow these calculations to be redone with, perhaps, one-half to one-third of the computer time, an enormous amount of computer time would still be needed. This time was mainly used in the minimization of σ to find the wave functions. Less than 5% of the time was used to find the energy of the final wave functions for the equilibrium separation with a Monte Carlo error that was less than chemical accuracy.

For the required amount of computer time to be reduced by more than the factor of two to three, three things would have to be done, separately or jointly. Firstly, the minimization would have to be made faster. Frequently, more than 500 calls had to be made to the simplex algorithm to find the best wavefunction. Dr. Coldwell is making continual progress along this line. Secondly, the number of Monte Carlo points required to evaluate the integrals accurately enough to allow meaningful minimizations would have to be reduced. Part II was a first step and suggested further steps to take along this line. Thirdly, better wave functions would have to be used. The form of $b(\vec{r})$ was not flexible enough to allow the wave function for the first energy band to have the same symmetry as the wave function for the second band: $b(\vec{r})$ should have been $\sum_{\tilde{G}} c_{\tilde{G}} e^{i\tilde{G}\cdot\vec{r}}$ ($\tilde{G} \equiv$ reciprocal lattice translation vector). Furthermore, the form of

$\tilde{u}_{\tilde{k}}(\tilde{r})$ became more inappropriate as $r_s \to 0$, more and more Monte Carlo points were required to minimize σ effectively.

This work showed that it is possible to use Monte Carlo and 2-electron wave functions to calculate the properties of bulk matter. It also gave encouraging signs, in Part II, that the $1/\sqrt{N}$ convergence of Monte Carlo can be beat in the evaluation of multi-dimensional quantum-mechanical expectation values.

APPENDIX A
THE BIASED SELECTION METHOD

INTRODUCTION

This appendix presents in one place for the first time detailed proofs, statements, and examples of the biased selection method of evaluating integrals and expectation values. Biased selection is, as the name suggests, a method of non-uniformly sampling an integrand, $f(x)$, in order to estimate $\int f(x)dx$. It is an extension of importance sampling, as given by Hammersley and Handscomb in reference [1], in the sense that it uses sums instead of integrals in order to exactly correct for the bias introduced by using a weight function, $g(x)$. In addition, biased selection allows one to use several simple weight functions simultaneously, one for each of several important regions of the integrand, in place of a single complicated weight function. Biased selection is harder to code than the Metropolis scheme, [1], [2], [3], but more flexible. Coldwell and Lowther used it in their calculations on the dihelium system [4].

A weight function, $g(x) > 0$, that mimics $f(x)$ can be used to lower the standard deviation in the Monte Carlo estimate of $\int f(x)dx$. For example, let

$$y = \int_0^x g(z)dz / \int g(z)dz$$

so that

$$\int f(x)dx = \int \frac{f(x(y))}{w(x(y))}\,dy,$$

(all integrals, from now on, are from 0 to 1, unless explicitly stated otherwise) where

$$w(x) \equiv g(x)/\int g(z)dz.$$

The estimate of the integral is then $\frac{1}{N}\sum \frac{f(x(y_i))}{w(x(y_i))}$ [1], where the y_i's are picked uniformly at random. When the exact value of $\int g(x)dx$ is used the above is importance sampling. It will be shown that biased selection gives similar results but does not require the exact evaluation of any integrals in order to exactly correct for the bias introduced by the nonuniform selection of the $\vec{x}$'s. This appendix will also show how several different w's can be averaged and used in place of a single w. This averaging allows the combination of several simple weight functions, rather than one complicated weight function, to sample the space adequately.

The methods detailed in this appendix often select one point from M points and repeat this N times to get the integral estimates. As $M\to\infty$ the biased selection method becomes importance sampling, owing to the fact that certain sums become integrals. It must be emphasized, and will be proved, that for M fixed, e.g., for M = 3 the method converges on the correct answer almost surely as $N\to\infty$.

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[1] Unless specifically indicated, all sums are from 1 to N.

I. ERROR ESTIMATION

The simple Monte Carlo estimate for a multi-dimensional integral is

$$I_N = \frac{1}{N}\sum f(\vec{x}_i) \tag{1}$$

where the $\vec{x}_i$'s are chosen uniformly at random. As $N\to\infty$, $I_N \to \int f(\vec{x})d\vec{x}$. Since the $\vec{x}_i$'s are random, sampling theory can be used to derive (for N large [5], [6]) an error estimate for I_N

$$\sigma = \{\frac{1}{N}\sum (f(\vec{x}_i) - I_N)^2\}^{\frac{1}{2}}/\sqrt{N}, \tag{2}$$

and an error estimate for $N\sigma^2$

$$\delta = \{\mu_4 - N^2\sigma^4\}^{\frac{1}{2}}/\sqrt{N}, \tag{3}$$

where $\mu_4 \equiv \frac{1}{N}\sum (f(\vec{x}) - I_N)^4$ [1], [2]. For these errors to assume their standard meanings (e.g. $|I_N - \int f(\vec{x})d\vec{x}| \leq \sigma$ approximately 68% of the time) then I_N and σ^2 must be approximately normally distributed about the values that they would take on if an infinite number of points were sampled, in this case $\delta \simeq \sqrt{2N}\,\sigma^2$ [1], [7], [8]. For simple Monte Carlo it is generally claimed that N should be greater than about 30 for the I_N's and greater than about 100 for the σ^2's to become almost normally distributed. For both biased selection and importance sampling, Eqs. (1), (2), and (3) are correct after the following changes: replace $f(\vec{x})$ by $f(\vec{x})/w(\vec{x})$, and select the $\vec{x}$'s according to $w(\vec{x})$ (in importance sampling this can be done by selecting y uni-

formly at random and then calculating $\bar{x}$, see introduction, in the case of biased selection the techniques of section III can be used). Biased selection requires fewer points than simple Monte Carlo does, in order to obtain accurate estimates of the integral and its error. It reduces σ by reducing its proportionality constant, not its inherent $1/\sqrt{N}$ dependence.

Restrictions must be placed on the integrand for σ and δ to be used as error estimates and maintain their common meanings. In particular, σ and μ_4 should exist and be bounded, and σ should tend to zero as $N\to\infty$.

It is suprisingly easy to violate these conditions. Consider the integral $\int x^{-\frac{1}{2}}dx$, it exists but σ and μ_4 are infinite. Numerically, this shows up as a σ that decreases as N increases, and then rises when a random point is chosen which comes much closer to the origin than all previous points; and as a δ which becomes much larger than σ as N is increased. If the proper weight function, e.g. $g(x) = \frac{1}{3}x^{-\frac{2}{3}}$, is chosen, the integral and σ can be interpreted in the usual way. In this case, the estimator is

$$\frac{1}{N}\sum (x_i^{-\frac{1}{2}})3x_i^{\frac{2}{3}} = \frac{3}{N}\sum x_i^{\frac{1}{6}}$$

and $\sigma, \sqrt{\frac{.5}{N}}$, and $\delta, \sqrt{\frac{.35}{N}}$, behave properly.

Suppose that nothing more were known about the integrand than that the largest contributions come from the origin. Observe what happens if the weight function favors the origin too much. For example, if $g(x) = \frac{1}{100}x^{-\frac{99}{100}}$, the integral becomes $\int \frac{1}{\sqrt{x(y)}}\left(\frac{1}{100}\, x(y)^{-\frac{99}{100}}\right)^{-1}dy$ which reduces to $100\int y^{49}dy$. The problem at $x = 0$ has become a problem at $x = 1$, $y = 1$, which, for good numerical results, still requires N

to be very large (this is now necessary in order to sample the region near x = 1 adequately, due to the low probability of placing a point there).

For a more useful example, consider evaluating the expectation value of a quantum mechanical Hamiltonian, H. Let E_0 be the eigenvalue of H, and $\Psi_t(x)$ be an approximate (normalized) eigenfunction. Then $H\Psi_t(x) = E(x)\Psi_t(x)$. Note that if $\Psi_t(x)$ were an exact eigenfunction that E(x) would be constant. However, for our purposes, suppose that $\Psi_t(x)$ is not an exact eigenfunction. We will assume that it is very good for $\Psi_t^2(x)$ large and very bad for $\Psi_t^2(x)$ small. If we use importance sampling and let the sampling function be $g(x) = \Psi_t^2(x) + \delta$ then the integral

$$\langle H - E_0 \rangle = \int [\Psi_t(x(y))(H - E_0)\Psi_t(x(y)) \left(\frac{\Psi_t^2(x(y)) + \delta}{\int(\Psi_t^2(z) + \delta)dz}\right)^{-1}]dy \qquad (4)$$

can be simplified and the estimator written as

$$\langle H - E_0 \rangle = \frac{1}{N}(1 + \delta) \sum \frac{E(x_i) - E_0}{1 + \delta/\Psi_t^2(x_i)}. \qquad (5)$$

It might appear that the best sampling function would be $\Psi_t^2(x)$ (i.e., $\delta = 0$), and, in fact, the Metropolis scheme uses this weight function. But, since most of the error in $H\Psi_t(x)$ is assumed to be for small values of $\Psi_t(x)$, say for $\Psi_t^2(x)$ less than a tenth of its maximum value (Ψ_M^2), then $|E(x) - E_0|$ will be the largest there. The error term will then be dominated by an area that is unlikely to be sampled (because $\Psi_t^2(x)$ is small). This means that a large N is needed to lower the error in $\langle H - E_0 \rangle$ because most of the points contribute little to the error while a very few make large contributions, since $w(\vec{x}_i)$ is very small for them. If δ were kept finite (say $\delta = .1\Psi_M^2$) instead of being set to zero, then the "misses" would be lowered in size to

$\frac{E(x) - E_0}{1 + \delta/\Psi_t^2(x)}$, instead of $E(x) - E_0$. This is, of course, exactly compensated for by the fact that there are now more of these "misses". Notice, in this case, that the term contributing to the error in $\langle H - E_0 \rangle$ is approximately halved. Each "miss" is cut by a factor of 4 in its contribution to σ, but there are twice as many of them. So, by sampling the "unimportant" regions more (i.e., no region is sampled with a probability that is less than, in this case, $.1\Psi_M^2$), σ can be reduced. It is interesting to observe that σ was reduced by using a seemingly worse weight function, and that a large number of points appear to be wasted because $(E(x) - E_0)/(1 + \delta/(\Psi_t^2))$ is (as $\Psi_t^2 \to 0$) zero for the most part.

II. BIASED SELECTION

In biased selection, a positive definite weight function, $g(\vec{x})$, is used to distribute the $\vec{x}_i$'s, with a probability $P_B(\vec{x}_i)$ (or probability density, as the case may be) which must be computable (explicit schemes for doing this are detailed in Section III). The bias is compensated for by dividing each $f(\vec{x}_i)$ in Eq. (1) by the relative probability of choosing $\vec{x}_i$,

$$w(\vec{x}_i) \equiv P_B(\vec{x}_i)/P_U(\vec{x}_i), \tag{6}$$

$P_U(\vec{x}_i)$ is the unbiased (uniform) probability of choosing $\vec{x}_i$. One should note, as the discussion develops, that $w(\vec{x}_i)$ can be a multi-valued function. This is because there can be more than one way to select any given $\vec{x}_i$ and each way can have a unique $w(\vec{x}_i)$ associated with it. The biased selection estimator is

$$I_N \equiv \frac{1}{N} \sum \frac{f(\vec{x}_i)}{w(\vec{x}_i)} . \tag{7}$$

To prove that Eq. (7) gives $\int f(\vec{x}) d\vec{x}$ as $N \to \infty$, the following can be done. Divide the integration region into T equal-volume hyper-cubes (label them T_a where a = 1, 2, ..., T) and select N $\vec{x}_i$'s, each with relative probability $w(\vec{x}_i)$, from it, N>>T [4]. Now, break up the sum into two sums -- one over the T_a's and the second over the points within a given T_a --

$$I_N = \frac{1}{N} \sum_{a=1}^{T} \sum_{i=1}^{n_a} f(\vec{x}_i)/w(\vec{x}_i).$$

To derive Eq. (8), two cases need to be considered. The case for the multi-valued $w(\vec{x}_i)$'s used herein is discussed in Section III. The case for single-valued $w(\vec{x}_i)$'s follows. As T becomes infinite, the volume of a given T_a becomes vanishingly small. Therefore, the continuity of $f(\vec{x})$ and $w(\vec{x})$ requires that $\frac{f(\vec{x}_i)}{w(\vec{x}_i)} \to \frac{f(\vec{x}_j)}{w(\vec{x}_j)}$ for all $\vec{x}_i$ and $\vec{x}_j$ within a given T_a.[1] Therefore, combining the n_a equivalent terms within each T_a gives

$$I_N \xrightarrow[T\to\infty]{} \frac{1}{N} \sum_{a=1}^{T} n_a \frac{f(\vec{x}_a)}{w(\vec{x}_a)} . \tag{8}$$

Since N>>T, the law of large numbers can be used to show that $\frac{n_a}{N} \to P_B(\vec{x}_a)$ almost surely, a.s., as $N\to\infty$. Also note that $P_U(\vec{x}_a) = \frac{1}{T}$. These two facts and Eq. (6) imply $n_a \xrightarrow{a.s.} N(\frac{1}{T})w(\vec{x}_a)$; which when substituted into Eq. (8) gives

$$I_N \xrightarrow[T\to\infty]{N\to\infty} \frac{1}{N} \sum_{a=1}^{T} N(\tfrac{1}{T})w(\vec{x}_a) \frac{f(\vec{x}_a)}{w(\vec{x}_a)} \qquad \text{(almost surely)}$$
$$= \frac{1}{T} \sum_{a=1}^{T} f(\vec{x}_a).$$

This is the definition of the Riemann integral in the limit of infinite T

$$I_N \xrightarrow[T\to\infty]{a.s.} \int f(\vec{x}) d\vec{x}.$$

Note that if $w(\vec{x})$ were equal to unity that the above proof reduces to a proof for simple Monte Carlo.

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[1] The results remain valid if $f(\vec{x})$ and $g(\vec{x})$ have a countably infinite set of regions over which they are continuous, but the explanations are too detailed for this paper's purpose.

The closer the weight function can be made to $f(\vec{x})$, the more constant $f(\vec{x})/w(\vec{x})$ will be; and, consequently, the smaller σ will be (approaching zero for non-negative $f(\vec{x})$ and $f(\vec{x})/w(\vec{x})$ absolutely constant). While $w(\vec{x}) = |f(\vec{x})|/\int|f(\vec{x})|d\vec{x}$ does minimize σ, to evaluate $w(\vec{x})$ one would have to know the integral that, by hypothesis, is not known. It should be cautioned that a bad weight function can greatly increase the number of points before Eqs. (2) and (3) accurately indicate how far I_N is from $\int f(\vec{x})d\vec{x}$. For example, if w concentrates the points in "unimportant" regions, the integral effectively becomes the integral of f(x) over these "unimportant" regions. The important regions will not be sampled for small N because of their small probability of being selected. Thus, the averages and error estimates are only for a part of the total integral being sought. This results in a low σ which could lead to the erroneous conclusion that I_N was close to $\int f(\vec{x})d\vec{x}$ instead of the correct conclusion that I_N was a good estimate of the integral of f over the "unimportant" regions. This misconception will not be revealed until N is large enough for the "important" regions to finally be sampled. (Note: For the important regions to eventually be sampled, in general, $g(\vec{x})$ must never be zero.)

Let us assume that we have an integrand, $f(\vec{x})$, with the locations of some peaks known and others unknown. Then a measure of the number of points making a significant contribution to the estimate of the integral is

$$N_{eff} \equiv \left[\sum \left|\frac{f(\vec{x}_i)}{w(\vec{x}_i)}\right|\right]^2 / \sum \left[\frac{f(\vec{x}_i)}{w(\vec{x}_i)}\right]^2. \tag{9}$$

The number of "effective" points can range from $N_{eff} = 1$, when one value of $f(\vec{x}_i)/w(\vec{x}_i)$ is much larger than the others (and therefore makes the major contribution to Eq. (7)), to $N_{eff} = N$, when all N values of $f(\vec{x}_i)/w(\vec{x}_i)$ are equal. Since it has been assumed that we do not know the location of all the peaks, it is undesirable to have $N_{eff} \simeq N$. This is because such a large N_{eff} can only be obtained by concentrating the points where peaks of the integrand were thought to lie. This concentration precludes any chance of selecting a point from one of the unknown peaks. A good weight function to use is $g(\vec{x}) = b(\vec{x}) + d$, where $b(\vec{x})$ incorporates, as much as possible, all of the known properties of the integrand and d is a constant. This way, if there exists some $\vec{x}_0$ where $f(\vec{x}_0)$ is large but was thought to be small (i.e. $b(\vec{x}_0)$ is small), then $\vec{x}_0$ still has a chance of being selected. The selection of this $\vec{x}_0$ causes N_{eff} to drop to approximately unity. The statistics of this run become highly suspect. However, the precipitous drop in N_{eff} tells us that we didn't know all of the regions in which $f(\vec{x})$ was large, and therefore, allows us to select a better $b(\vec{x})$, enabling us to eventually find the correct value of $\int f(\vec{x})d\vec{x}$. Notice that it was the presumably wasted points that enabled us to locate the unsuspected peak.

In practice we have found that when $N_{eff} < .2N$ it pays to improve $b(\vec{x})$, and that for $N_{eff} > .3N$ it pays to sample more of the regions where $b(\vec{x})$ is small (increase d).

The following example illustrates this. Suppose that $f(x)$ has two equal peaks (where $f(x) = 10^6$) that each extend over a length equal to .001 (where the total integrand is from $x = 0$ to $x = 1$) and is one elsewhere. Then consider a $b(x)$ that equals f at one peak and zero

elsewhere. If $d \simeq 1$, then information sampling would have roughly a chance in 1000 of sampling where $b(x) = 0$, and then only a chance in 1000 of that point hitting the second peak. Therefore, for $N \simeq 10^4$ there is a 99% chance of not sampling the second peak. This results in an $I_N \simeq \frac{1}{2}\int f(x)dx$ and an $N_{eff} \sim 10^4$. If N is increased to 10^6, there is a 73% chance of hitting the second peak and getting $I_N \simeq \int f(x)dx$ and an $N_{eff} \simeq 4$. Finally, if d is increased to 5000, then there is approximately an 83% chance of selecting a point where $b(x) = 0$. Then for $N \simeq 10^4$, roughly 8 points would hit the second peak giving $I_N \simeq \int f(x)dx$ and $N_{eff} \simeq 30$. So, with fewer points than was required for $d/b \ll 1$, the estimates were improved. Furthermore, enough evidence has been gathered to alter $b(x)$ so that it contains the second peak.

The Metropolis scheme for evaluating expectation values, e.g. $\langle h \rangle = \int h(\vec{x}) f(\vec{x}) d\vec{x} / \int f(\vec{x}) d\vec{x}$, uses $|f(\vec{x})|$ to sample the integrand, but does not give an estimate for $\int f(\vec{x}) d\vec{x}$ as biased selection does. This weight function gives the minimum error in $\langle h \rangle$ only when $h(\vec{x}) = 1$. The Metropolis method is easier to code than biased selection, since there is no need to calculate probabilities, biases, or weight functions, and since it is very simple to generate $\vec{x}_{i+1}$ from $\vec{x}_i$. But each $\vec{x}_{i+1}$ is strongly correlated with each $\vec{x}_i$. This means that a large number of functional evaluations must be discarded before the remaining can be used to estimate the integrand. However, all of the functional evaluations in biased selection are statistically independent, giving the biased selection method an advantage when N must be small. By increasing the complexity of the Metropolis scheme it is possible to use a different weight function, $g(x)$. The integral, $\int g(x)dx$, generally is not evaluated in the Metropolis scheme. For this reason the Metro-

polis scheme doesn't have the ability to use multiple weight functions simultaneously. This gives biased selection an edge in evaluating the integrals of multi-peaked functions. Biased selection can use several weight functions to generate a set of points which are not as concentrated as those generated by Metropolis' method. This set of points (and associated $w(\vec{x}_i)$'s) can be saved and used to evaluate the integrals of a wider variety of integrands -- providing useful correlations in the integral estimates and saving the expense of generating a new set of $\vec{x}_i$'s and $w(\vec{x}_i)$'s.

The class of functions which can be used for $w(\vec{x})$ in Eq. (7) can be greatly extended to include, not only relative probabilities, but also weighted sums of relative probabilities. For example, a point, $\vec{x}$, can be selected by two different schemes -- one which has biased and unbiased probabilities of selecting an $\vec{x}$ of $P_{B1}(\vec{x})$ and $P_{U1}(\vec{x})$, the second which has biased and unbiased probabilities of selecting an $\vec{x}$ of $P_{B2}(\vec{x})$ and $P_{U2}(\vec{x})$. This can happen in cases where one scheme rarely selects points from a region that the second scheme frequently does. It will be shown that if the point is selected by one method some fraction, p_1, of the time and by the second method the remainder, $p_2 = 1 - p_1$, of the time, then

$$\overline{w}(\vec{x}_p) = p_1 \frac{P_{B1}(\vec{x}_p)}{P_{U1}(\vec{x}_p)} + p_2 \frac{P_{B2}(\vec{x}_p)}{P_{U2}(\vec{x}_p)}$$

$$= p_1 w_1(\vec{x}_p) + p_2 w_2(\vec{x}_p) \qquad (10)$$

is the correct function to use in place of $w(\vec{x})$ in Eq. (7). (The $\overline{w}(\vec{x}_p)$ in Eq. (10) is the relative probability of choosing $\vec{x}_p$ only if $P_{U1}(\vec{x}_p) = P_{U2}(\vec{x}_p)$.) It should be emphasized that the w in Eq. (6) and the $\overline{w}$ in

Eq. (10) represent totally different ways of selecting points. In Eq. (6) each of the points is selected using the same weight function $g(\vec{x})$. But in Eq. (10) each of the $\vec{x}_i$'s is chosen either using g_1 (in which case this point, $\vec{x}_{1i}$, would be used to evaluate the contribution, $f(\vec{x}_{1i})/\overline{w}(\vec{x}_{1i})$, to the sum) or using g_2 (giving $f(\vec{x}_{2i})/\overline{w}(\vec{x}_{2i})$) but not by both.

The following shows that $\overline{w}(\vec{x})$ does indeed give the correct results. First Eq. (7), with Eq. (10) used in place of Eq. (6), is broken into two sums, one is over the points chosen by w_1 and the second is over the points chosen w_2,

$$I_N = \frac{1}{N}\Big[\sum_{i=1}^{p_1 N} f(\vec{x}_{1i})/\overline{w}(\vec{x}_{1i}) + \sum_{i=1}^{p_2 N} f(\vec{x}_{2i})/\overline{w}(\vec{x}_{2i})\Big].$$

Breaking these into a sum over the T_a's and a sum over f_{ia} (the f_{ia}'s are the f_i's within a given T_a) and then using continuity to carry out the sum over the f_{ia}'s gives

$$I_N \xrightarrow[T\to\infty]{a.s.} \frac{1}{N}\sum_{a=1}^{T}\left[Np_1 w_1(\vec{x}_a)/T + Np_2 w_2(\vec{x}_a)/T\right] f(\vec{x}_a)/\overline{w}(\vec{x}_a)$$

$$= \frac{1}{T}\sum_{a=1}^{T} f(\vec{x}_a)$$

$$\xrightarrow[T\to\infty]{a.s.} \int f(\vec{x})\,d\vec{x} \ .$$

What's more, this estimator is still correct if some of the T_a's cannot be reached by one or the other of the weight functions, as long as each T_a is reachable by at least one of the weight functions. For example, if T_a was unreachable by w_1 (i.e., $w_1(\vec{x}_a) = 0$) then $f(\vec{x}_{1a})/\overline{w}(\vec{x}_{1a}) = 0$, since there would not be any $\vec{x}_{1a}$'s. Furthermore,

$$f(\vec{x}_{2a})/\overline{w}(\vec{x}_{2a}) = (Np_2w_2(\vec{x}_{2a})/T)f(\vec{x}_{2a})/(0 + p_2w_2(\vec{x}_{2a}))$$

$$= (N/T)f(\vec{x}_{2a})$$

and everything follows through as before. All of these methods have the same biases that simple Monte Carlo does: they are exact as $N\to\infty$ and their errors are proportional to $1/\sqrt{N}$. The advantage of these methods is that they can greatly reduce the proportionality constant for $1/\sqrt{N}$.

III. DETAILED BIAS SELECTION SCHEMES

The following will give explicit details on how to choose an $\vec{x}_i$ with biased probability $P_B(\vec{x}_i)$, once a positive definite $g(\vec{x})$ has been decided upon. We will not give recipes for finding the best $g(\vec{x})$ for a given problem, but the "physics" of the situation frequently suggests which regions are the "important" ones. First, N_s $\vec{x}_i$'s are selected uniformly at random, and a $g(\vec{x}_i)$ is calculated for each of them. Next, a series of partial sums is calculated

$$S_0 = 0$$

$$S_i = S_{i-1} + g(\vec{x}_i)$$

$$S_{N_s} = \sum_{i=1}^{N_s} g(\vec{x}_i).$$

A random number, R, is then chosen uniformly from the interval R = 0 to R = S_{N_s}. Then a "p" is determined such that

$$S_{p-1} \leq R \leq S_p.$$

Finally, $\vec{x}_p$ is picked and the remaining $N_s - 1$ $\vec{x}_i$'s are discarded. The biased probability of choosing $\vec{x}_p$ is proportional to $g(\vec{x}_p)$

$$P_B(\vec{x}_p) = g(\vec{x}_p)/S_{N_s}, \tag{11}$$

while the uniform probability of choosing $\vec{x}_p$ is

$$P_U(\vec{x}_p) = \frac{1}{N_s}. \tag{12}$$

The relative probability of choosing $\vec{x}_p$ is found by substituting Eq. (11) and Eq. (12) into Eq. (6) to get

$$w(\vec{x}_p) = g(\vec{x}_p)/(\frac{1}{N_s} S_{N_s}). \tag{13}$$

Note that, since S_{N_s} depends on which set of N_s $\vec{x}_i$'s is selected, $w(\vec{x}_p)$ is a multi-valued function. But also notice that $w(\vec{x}_p)$ is distributed about $\frac{g(\vec{x}_p)}{\int g(\vec{x})d\vec{x}}$ in exactly the same fashion, and for exactly the same reasons, as $\frac{1}{N_s} S_{N_s}$ is distributed about $\int g(\vec{x})d\vec{x}$--leading to the following interesting consequences. Consider what happens to $\frac{1}{N} \sum_{i=1}^{n_a} \frac{f(\vec{x}_i)}{w(\vec{x}_i)}$ as $T \to \infty$ (causing $T_a \to 0$) and as n_a (and therefore N) $\to \infty$. As in the derivation of Eq. (8) continuity of $f(\vec{x})$ and $g(\vec{x})$ demands that

$$\frac{1}{N} \sum_{i=1}^{n_a} \frac{f(\vec{x}_i)}{w(\vec{x}_i)} \to \frac{1}{N} \frac{f(\vec{x}_a)}{g(\vec{x}_a)} \sum_{i=1}^{n_a} \frac{1}{N_s} \sum_{j=1}^{N_s} g(\vec{x}_j)$$

$$\xrightarrow[n_a \to \infty]{a.s.} \frac{1}{N} \frac{f(\vec{x}_a)}{g(\vec{x}_a)} n_a \int g(\vec{x})d\vec{x}.$$

But note that

$$w(\vec{x}_a) \xrightarrow[N_s \to \infty]{a.s.} \frac{g(\vec{x}_a)}{\int g(\vec{x})dx}.$$

Therefore, as T becomes infinite

$$\frac{1}{N} \sum_{i=1}^{n_a} \frac{f(\vec{x}_i)}{w(\vec{x}_i)} \xrightarrow[n_a \to \infty]{a.s.} n_a \frac{f(\vec{x}_a)}{w(\vec{x}_a)},$$

and as $N \to \infty$, $I_N \to \int f(x)dx$ for all values of N_s. For small values of N_s the size of σ is partly due to the sampling variance of S_{N_s} and partly due to the fact that g does not imitate f perfectly. Note that for $N_s = 1$, simple Monte Carlo is exactly recovered, while for $N_s \to \infty$, importance sampling is obtained. The best value of N_s depends on how closely g mimics f and on the relative costs of evaluating g and f.

Frequently, it is more convenient to use two (or more) independent weight functions, g_1 and g_2 [4].

> An example of this is the calculation of the energy integral for an H_2^+ molecule. The potential energy causes the integrand to be singular for two separate instances -- when the separation of the electron from either of the two nuclei goes to zero. Then one weight function could be designed to follow the singularity due to the electron's close approach to one nucleus, and the second weight function could follow the singularity due to the electron's close approach to the second nucleus. Neither could be suitably used by itself, because the remaining singularity would make σ excessively large.

Then g_1 could be used (in the same way g was) with probability p_1 to select a fraction, p_1N, of the points, and g_2 could be used to select the remaining p_2N points, $p_2 = 1-p_1$. Since the probability of selecting g_1 (g_2) is p_1 (p_2), and the probability of selecting $\vec{x}_p$ once g_1 (g_2) has been selected is $g_1(\vec{x}_p)/S_{1N_s}$ ($g_2(\vec{x}_p)/S_{2N_s}$), the total biased probability of choosing $\vec{x}_p$ is

$$P_B(\vec{x}_p) = P(g_1)P(\vec{x}_p|g_1) + P(g_2)P(\vec{x}_p|g_2)$$

$$= p_1 g_1(\vec{x}_p)/S_{1N_s} + p_2 g_2(\vec{x}_p)/S_{2N_s}, \qquad (14)$$

where $P(x_p|g_1)$ is the probability that $\vec{x}_p$ is chosen given that g_1 was. The uniform probability of choosing $\vec{x}_p$ was $\frac{1}{N_s}$; therefore, the relative probability of choosing $\vec{x}_p$ is

$$\overline{w}(\vec{x}_p) = p_1 g_1(\vec{x}_p)/(\tfrac{1}{N_s} S_{1N_s}) + p_2 g_2(\vec{x}_p)/(\tfrac{1}{N_s} S_{2N_s}). \qquad (15)$$

Note that Eq. (15) is just a particular case of Eq. (10).

One problem with biasedly selecting an $\vec{x}_p$ by the above methods is that σ can be increased by rare occurrences [9]. For example, suppose a large number of the N_s $\vec{x}_i$'s happened to be selected uniformly at random in some small, but "important", region, T_a. Then if $\vec{x}_p$ happened to be within T_a, $P_B(\vec{x}_p)$ would be anomalously small because a large number of the $g(\vec{x}_i)$'s would be the same size as $g(\vec{x}_p)$. This would, in turn, cause $w(\vec{x}_p)$ to be small; which would make $f(\vec{x}_p)/w(\vec{x}_p)$ much larger than the other contributions, $f(\vec{x}_i)/w(\vec{x}_i)$, to Eq. (7) from T_a where more probable sets of $\vec{x}_i$'s were selected. The effect of the anomalous behaviour of $f(\vec{x}_i)/w(\vec{x}_i)$ within an "important" T_a on σ can be mediated by the following averaging process. Once an $\vec{x}_p$ has been chosen by $g(\vec{x})$ and a biased probability of selecting $\vec{x}_p$, $P'_B(\vec{x}_p)$, has been calculated, then select a new set of N_s $\vec{x}_i$'s by keeping $\vec{x}_p$ and reselecting the other N_s-1 $\vec{x}_i$'s. Then calculate the new $P_B(\vec{x}_p)$, call it $P''_B(\vec{x}_p)$, assuming that $\vec{x}_p$ was also chosen in the second case. The biased probability to use in Eq. (6) will be

$$P_B(\vec{x}_p) = \frac{1}{2}[P'_B(\vec{x}_p) + P''_B(\vec{x}_p)]$$

$$= \frac{1}{2}\left[\frac{g(\vec{x}_p)}{g(\vec{x}_i) + \ldots + g(\vec{x}_p) + \ldots + g(\vec{x}_{N_s})} + \frac{g(\vec{x}_p)}{g(\vec{x}'_i) + \ldots + g(\vec{x}_p) + \ldots + g(\vec{x}'_{N_s})}\right].$$

The uniform probability of choosing $\vec{x}_p$ is still $1/N_s$, and therefore, the relative probability of choosing $\vec{x}_p$ is

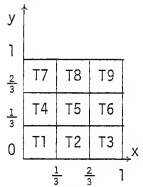
$$w(\vec{x}_p) = P_B(\vec{x}_p)/(\tfrac{1}{N_s}).$$

Great care must be taken to perform the averages precisely as indicated in order to be sure that the biased probability is correct. It is only when P_B is calculated correctly that w, as defined, corrects for the biasedly selected $\vec{x}_i$'s. For example, although it might reduce the variance of P_B to average the two denominators and then invert them, the resulting number would no longer be the biased probability of selecting $\vec{x}_p$. It should be noted that this must be done for every $\vec{x}_p$, and as many $P_B(\vec{x}_p)$'s can be averaged as desired. Furthermore, $f(\vec{x})$ is only calculated one time, for each $\vec{x}_p$. This offers an inexpensive way (when $f(\vec{x})$ is expensive to evaluate while $g(\vec{x})$ is not) to reduce the dispersion introduced by the above methods of calculating $P_B(\vec{x})$.

IV. EXAMPLES WITH NUMBERS

This section provides an example that explicitly demonstrates the subtleties of the biased selection methods, and how the biased probabilities must be calculated and averaged in order to obtain the correct results. Furthermore, it demonstrates that the results are exact, even for finite N_s.

First, suppose the value of a two-dimensional integral, $\int f(x,y)dxdy$, is desired. Assume for simplicity that the unit square, over which the integral is being evaluated, can be divided into nine equal-area sub-squares, T_a's, so that $f(x,y)$ is a constant in each one of them. Label the sub-squares as follows:



and let the integrand be

$$f(x,y) = 0 \qquad (x,y) \notin T9$$
$$= 9 \qquad (x,y) \in T9 . \tag{16}$$

Three different Monte Carlo integrations (simple, biased selection without averaging, and biased selection with averaging) will be performed with this function to see how close each comes to the answer, 1. This allows a comparison of the three methods with one another.

First, simple Monte Carlo: each of the points, (x,y)'s, will be selected uniformly at random from the unit square. Therefore, each of the T_a's will be equally likely to be sampled, with a probability of $\frac{1}{9}$. If a large enough number of points, N, is used to evaluate Eq. (7) then

$$I_N = \frac{1}{N}[N\frac{1}{9}f(T1) + N\frac{1}{9}f(T2) + \ldots + N\frac{1}{9}f(T9)] = 1$$

and

$$\langle f^2 \rangle_N = \frac{1}{N}[N\frac{1}{9}f^2(T1) + \ldots + N\frac{1}{9}f^2(T9)] = 9,$$

where, when $\vec{x} \in T1$, $f(\vec{x})$ is written $f(T1)$. Using Eq. (3) and the two above equations give

$$\sigma \simeq (\frac{8}{N})^{\frac{1}{2}}.$$

Second, bias selection without averaging: two points will be selected from which one point will be selected with a biased probability determined by some g(x,y), as in Eq. (11). This point will then be used to evaluate one of the N contributions to Eq. (6). Let the weight function be

$$\begin{aligned} g(x,y) &= .01 && \text{for } (x,y) \in T2, T4, T7, \text{ or } T8 \\ &= .09 && \text{for } (x,y) \in T1, T3, T5, \text{ or } T6 \\ &= .81 && \text{for } (x,y) \in T9. \end{aligned} \qquad (17)$$

If the points are selected uniformly at random from the unit square there will be nine equally probable cells they can be selected from. This gives 9(9) or 81 possible ways of choosing two points from the nine cells. Therefore, the probability of selecting two points from

a particular pair of cells is $\frac{1}{81}$. Only if the pair of points is chosen from one of the seventeen pairs of cells in Table I can a non-zero contribution be made to Eq. (7). The contribution to Eq. (7) from each given value of $f(\vec{x})/w(\vec{x})$ is

> N × (Probability of selecting a pair with given w) × (Bias probability of selecting the point from T9--from the given pair of points--with the given w) × (f(x)/w(x)).

Using this and Table I yields

$$I_N = \frac{1}{N}[N(\frac{1}{81})(1)(\frac{9}{1}) + N(\frac{8}{81})(.9)(\frac{9}{1.8}) + N(\frac{8}{81})(.9878)(\frac{9}{1.9756})] = 1$$

$$\langle(f/w)^2\rangle_N = 5.2469.$$

Using Eq. (3) and the two above equations gives

$$\sigma = (\frac{4.2469}{N})^{\frac{1}{2}} .$$

The ratio of the error estimate for simple Monte Carlo to the error estimate for biased selection without averaging is approximately .73. For the above integrand and weight function biased selection without averaging gives a 27% smaller error estimate than simple Monte Carlo.

Third, biased selection with averaging: after a point has been selected from a pair as in the second method a new pair of points is generated by keeping the previously selected point and selecting the second point uniformly at random from the unit square. The two relative probabilities obtained from the two pairs of points will then be averaged, as in Eq. (15), to obtain w(x, y). Table II, when used in conjunction with Table I, can be used to calculate I_N and σ

Table I. The necessary probabilities and relative probabilities for the evaluation of Eq. (7) (using Eqs. (6), (13), (16), and (17)) are given.

17 pairs that can give non-zero f(x,y)	[g(1)+g(2)], 1 (2) is for point from 1st (2nd) cell of pair	Probability of selecting the given pair with the given w	Bias probability of selecting point from T9, given the pair and w	Uniform probability of selecting point from T9, given the pair and w	w for case where selected point was from T9
T9 T9	1.62	$\frac{1}{81}$	1	1	$\frac{1}{1} = 1$
T9 T1 T9 T3 T9 T5 T9 T6 T1 T9 T3 T9 T5 T9 T6 T9	.90	$\frac{8}{81}$	$\frac{.81}{.90} = .9$	$\frac{1}{2}$	$\frac{.9}{.5} = 1.8$
T9 T2 T9 T4 T9 T7 T9 T8 T2 T9 T4 T9 T7 T9 T8 T9	.82	$\frac{8}{81}$	$\frac{.81}{.82} \simeq .9878$	$\frac{1}{2}$	$\frac{.9878}{.5} = 1.9756$

Table II. The second relative probability of selecting the same point by a different path.

Possible regions to rechoose 2nd point from	Probability of selecting point from given region with given w_2	w_2 where one point is in T9 and the other is in given region	Average of w_1 and w_2, where w_1 has the indicated values		
			$\frac{w_2 + 1}{2}$	$\frac{w_2 + 1.8}{2}$	$\frac{w_2 + 1.9756}{2}$
T9	$\frac{1}{9}$	1	1	1.4	1.4878
T1 T3 T5 T6	$\frac{4}{9}$	$\frac{.81}{\frac{1}{2}(.81+.09)} = 1.8$	1.4	1.8	1.8878
T2 T4 T7 T8	$\frac{4}{9}$	$\frac{.81}{\frac{1}{2}(.81+.01)} \simeq 1.9756$	1.4878	1.8878	1.9756

$$I_N = \frac{1}{N}[N(\frac{1}{81})(1)(\frac{4}{9})(\frac{9}{1.4} + \frac{9}{1.4878}) + N(\frac{1}{81})(1)(\frac{1}{9})(\frac{9}{1}) +$$

$$N(\frac{8}{81})(.9)(\frac{4}{9})(\frac{9}{1.8} + \frac{9}{1.8878}) + N(\frac{8}{81})(.9)(\frac{1}{9})(\frac{9}{1.4}) +$$

$$N(\frac{8}{81})(.9878)(\frac{4}{9})(\frac{9}{1.8878} + \frac{9}{1.9756}) + N(\frac{8}{81})(.9878)(\frac{1}{9})(\frac{9}{1.4878})]$$

$$= 1$$

and

$$<(\frac{f(\vec{x})}{w(\vec{x})})^2>_N = 5.1144.$$

Using Eq. (3) and the two above equations gives

$$\sigma = (\frac{4.1144}{N})^{\frac{1}{2}}$$

The ratio of the error estimate for biased selection with averaging to biased selection without averaging is approximately .98. For the above integral and weight function biased selection with averaging gives a 2% smaller estimate than biased selection without averaging. Note that it also approximately doubles the biased selection overhead. How useful this averaging is depends on the relative expense of evaluating f and w and is therefore highly dependent on the particular problem. The more expensive f is to evaluate, relative to w, the smaller the improvement in σ needs to be for the averaging to pay for itself.

V. HYDROGEN MOLECULE

As a final example, this section contains a calculation of the ground state energy, using the eleven-term James-and-Coolidge wave function [10], for dihydrogen at a nuclear separation of 1.4 Bohr radii (the potential minimum). Note that James and Coolidge did not use Monte Carlo methods. Instead, they analytically evaluated the more than 140 integrals involved. This example incorporates a number of biased selection methods which can also, in principle, be used for other atomic and molecular systems.

The following is useful for calculating the required relative probabilities. The probability density function, $\rho(x)$, of a random variable, x, gives the probability of selecting a given x, x_0, between x_0 and $x_0 + dx$ as

$$P(x_0) = \rho(x_0)dx. \tag{18}$$

Frequently, the density function $\rho_1(h(x))$, for a function, h(x), of a random variable, x (whose probability function is known to be $\rho_0(x)$), is desired. In this case [7]

$$\rho_1(h(x)) = \rho_0(x) \left| \frac{dx}{dh(x)} \right|. \tag{19}$$

For the special case where x is a random variable, R_i, which is selected uniformly at random from the interval $R_i = 0$ to $R_i = 1$, the probability density function is $\rho_0(R_i) = 1$, therefore, the probability density function for some

function, h(R), of this random variable is

$$\rho_1(h(R)) = 1\left|\frac{dR}{dh(R)}\right|. \qquad (20)$$

As an illustration, consider the calculation of the relative probability for randomly selecting spherical coordinates:

$$r = R_1 M,\ \mu = 2R_2 - 1,\ \phi = 2\pi R_3 \qquad (21)$$

(R_i's ≡ different random numbers between zero and one, M ≡ the maximum r, μ ≡ the cosine of the angle between r and the z-axis, and φ ≡ the angle between the projection of r in the x-y plane and the x-axis). Selecting spherical coordinates randomly would have an advantage over selecting cartesian coordinates randomly when, for example, the integrand was basically a function of r (e.g., the r^2 part of P_U cancels the 1/r singularity of the potential). Since the R_i's are chosen uniformly at random and the spherical coordinates are functions of R (e.g., r = h(R) = R_1M), the probability density functions are, using Eqs. (20) and (21),

$$\rho_1(r) = 1/M,\ \rho_2(\mu) = 1/2,\ \rho_3(\phi) = 1/2\pi. \qquad (22)$$

From Eqs. (18) and (22) the biased probability of selecting these coordinates is

$$P_B(r, \mu, \phi) = \frac{dr}{M}\ \frac{d\mu}{2}\ \frac{d\phi}{2\pi}. \qquad (23)$$

The uniform probability of selecting these coordinates is the ratio of the infinitesimal volume around them to the total volume, V,

$$P_U(r, \mu, \phi) = r^2 dr d\mu d\phi / V. \qquad (24)$$

Finally, the relative probability of randomly selecting spherical coordinates is, using Eqs. (6), (23) and (24),

$$w_{sphere}(x) \equiv w_{sphere}(r, \mu, \phi) = V/(4\pi Mr^2). \tag{25}$$

The integration region will be a large box of length Lx (Ly or Lz) in the x (y or z) direction. The box is large enough to contain all of the region where $\Psi(x)$ is essentially non-zero. Keeping the box finite allows the random numbers to be generated easily without introducing singularities. The two nuclei are fixed on the z-axis with the point halfway between them coincident with the box's center. The coordinates of the first electron will be selected in four ways and those of the second in five (four ways being the same as for the first electron). One way, which guarantees that the entire integration region is sampled, is to select the electron's coordinates uniformly at random from the box. A second way, which accounts for the rather large probability of the electrons being there, is to select the electron's coordinates with respect to the midpoint between the nuclei. Third and fourth ways, which account for the nuclear-electron correlation, are to select the electron's coordinates with respect to one or the other of the two nuclei. The fifth way, for the second electron, which accounts for the singularity due to the electron-electron potentials, is to select the second electron's coordinates with respect to the first electron's.

An electron's coordinates can be selected uniformly at random from the box by letting its coordinates be

$$x = R_1 Lx, \; y = R_2 Ly, \; z = R_3 Lz.$$

Using Eqs. (6) and (20) gives the expected relative probability of selecting the coordinates uniformly at random from the box of

$$w_B(\vec{x}) = 1.$$

An electron's coordinates can be selected with respect to the box's center by letting

$$r_c = \sqrt{R_1}M_c,\ \mu = 2R_2 - 1,\ \phi = R_3 2\pi \tag{26}$$

($r_c \equiv$ the electron's distance from the center). Using Eqs. (20) and (26) and letting $h_1(R_c) = \sqrt{R_1}M_c$ gives the following probability density function

$$\rho_1(r_c) = 2\sqrt{R_1}/M_c. \tag{27}$$

With Eqs. (18),(22) and (27), the biased probability of selecting r_c, μ, and ϕ can be calculated; then, using Eqs. (6) and (24), the relative probability of selecting the electron's coordinates with respect to the center is calculated to be

$$w_c(r_c, \mu, \phi) = V/(2\pi M_c^2 r_c). \tag{28}$$

An electron's coordinates can be selected with respect to either of the two nuclei by using a weight function, g(y). An r_{N1} is selected by requiring

$$A(R_1) \equiv R_1 \int_0^{\infty} g(y)dy = \int_0^{r_{N1}} g(y)dy. \tag{29}$$

The remaining coordinates, μ and ϕ, are selected as in Eq. (26). The probability density function for r_{N1} can be calculated using Eq. (10), if it is first realized that r_{N1} is a function of A which is, in turn,

a function of R. Using Eqs. (19),(20) and (29) leads to

$$\rho_1(r_{N1}) = \rho(A)\left|\frac{dA}{dr_{N1}(A)}\right|$$

$$= 1\left|\frac{dR_1}{dA(R_1)}\right|\left|\frac{dA}{dr_{N1}(A)}\right|$$

$$= \left|\frac{g(r_{N1})}{\int_0^\infty g(y)dy}\right|. \tag{30}$$

Therefore, using Eqs. (18), (26), and (30),

$$P_B(r_{N1}, \phi, \mu) = \frac{g(r_{N1})dr_{N1}d\phi d\mu}{4\pi\int_0^\infty g(y)dy}, \tag{31}$$

and the relative probability of selecting the electron's coordinates with respect to the first and second nucleus, respectively, can be calculated (using Eqs. (6), (24), and (31)) to be

$$w_{N1}(r_{N1}, \phi_1, \mu_1) = \frac{g(r_{N1})V}{4\pi r_{N1}^2\int_0^\infty g(y)dy}$$

and

$$w_{N2}(r_{N2}, \phi_2, \mu_2) = \frac{g(r_{N2})V}{4\pi r_{N2}^2\int_0^\infty g(y)dy}. \tag{32}$$

In practice, a good weight function is $g(x) = x^2\Psi^2(x)$, where $\Psi^2(x)$ is, in general, the Hartree-Fock nuclear-electronic correlation function (in the example $\Psi(x)$ is the ground state hydrogen wave function). The Hartree-Fock functions can be found in tables such as reference [11]. Note that the x^2 cancels the r_{N1}^2 in Eq. (32) and that Ψ follows the system's wave function quite well for large nuclear separations. To greatly lessen the amount of computer time required to biasedly select an r_{N1}, $x^2\Psi^2(x)$ is evaluated at some number of points, say K, and g(x)

is formed by connecting these K values by line segments. To determine an r_{N1}, $R_1 Q_K$ ($Q_i \equiv \int_0^{x_i} g(x)dx = \frac{1}{2}\sum_{j=1}^{i}(g_j + g_{j-1})(x_j - x_{j-1})$, and each x_j is one of the K used to evaluate $x_i^2\Psi^2(x_i)$) is calculated, and then a p is located such that

$$Q_p \leq R_1 Q_K \leq Q_{p+1};$$

then

$$r_{N1} = x_p - g_p/\Delta + [g_p^2 + 2(\Delta)Q_\delta]^{\frac{1}{2}}/\Delta$$

$$(\Delta \equiv \frac{g_{p+1} - g_p}{x_{p+1} - x_p} \text{ and } Q_\delta \equiv Q_{p+1} - Q_p).$$

If r_{N1} is not one of the K x_i's then $g(r_{N1})$ in Eq. (32) is

$$g(r_{N1}) = g_p + \frac{r_{N1} - x_p}{x_{p+1} - x_p}(g_{p+1} - g_p).$$

Since what happens as an electron approaches a nucleus closely is of interest, g(r) in Eq. (32) is altered slightly at the origin--it is made greater than zero, usually we take g(0) = g(1)--to make it more probable to place an electron close to the nucleus.

The second electron's coordinates can be selected with respect to the first's as in Eq. (26), with M_C replaced by M_E. Therefore, the relative probability of selecting the second electron's coordinates with respect to the first's is

$$w_E(r_E, \phi, \mu) = V/(2\pi M_E^2 r_E).$$

Note that r_E, in $w_E(\vec{x})$, is exactly what is needed to account for the singularity of the electron-electron potential.

If each of these methods is used with equal probability then

$$\overline{w}(\vec{x}_1, \vec{x}_2) = \frac{1}{4}[w_B(\vec{x}_1) + w_c(\vec{x}_1) + w_{N1}(\vec{x}_1) + w_{N2}(\vec{x}_1)] \times$$
$$\frac{1}{5}[w_B(\vec{x}_2) + w_c(\vec{x}_2) + w_{N1}(\vec{x}_2) + w_{N2}(\vec{x}_2) + w_E(\vec{x}_2)]. \qquad (33)$$

If desired, one more averaging can be done

$$\overline{w}'(\vec{x}_1, \vec{x}_2) = \frac{1}{2}[\overline{w}(\vec{x}_1, \vec{x}_2) + \overline{w}(\vec{x}_2, \vec{x}_1)].$$

The numbers in Table III were calculated using the relative probability in Eq. (33). The 10,000 point estimate required 14 seconds of Amdahl 470 time, and gave a .002 Rydberg accuracy. The calculation of <T> serves as a check that $\nabla\Psi$ was calculated properly, while the calculation of <V> serves as a check that the relative probabilities were evaluated correctly. Note that <H> being correct does not guarantee that the relative probabilities are correct. This is because $H\Psi_i \simeq E\Psi_i$ for all i, and therefore,

$$<H> = E(\sum\Psi_i^2/w_i/\sum\Psi_i^2/w_i) = E$$

regardless of the w_i's used. It is interesting to note, by comparison, that an unbiased Monte Carlo estimate for 10,000 points has an $N_{eff} < 2$, <T> = 2.6941, <V> = -7.3062, and <H> = -2.4828. In addition, the error estimates are unreliable - instead of decreasing as $1/\sqrt{N}$ they remained constant from N = 5,000 to N = 10,000. This is because smaller and smaller interparticle separations are sampled as N is made larger and larger. Even though these separations are sampled the least frequently they make the largest contributions. These contributions are increasing enough, as N increases, so that they keep σ from dropping.

Table III. Results for the H_2 molecule using the 11-term James-and-Coolidge wave function for a nuclear separation of 1.4 Bohr radii.

Number of Monte Carlo points			σ		σ		σ
100	N_{eff}	21.2		26.0		21.2	
	T	2.277	.086	2.344	.083	2.369	.099
	V	-4.40	.28	-4.16	.44	-4.75	.39
	H	-2.354	.019	-2.369	.015	-2.350	.033
200	N_{eff}	43.6		45.0		41.5	
	T	2.333	.069	2.339	.062	2.273	.070
	V	-4.69	.54	-3.94	.28	-4.90	.28
	H	-2.361	.017	-2.3520	.0097	-2.336	.020
400	N_{eff}	81.2		94.7		87.2	
	T	2.306	.049	2.340	.038	2.271	.046
	V	-5.02	.44	-4.16	.21	-4.85	.21
	H	-2.361	.013	-2.3352	.0069	-2.355	.015
10,000	N_{eff}					2222.0	
	T					2.3475	.0089
	V					-4.682	.055
	H					-2.3446	.0023

Three independent runs are tabulated. $N_{eff} \equiv (\sum \Psi_i H\Psi_i/w_i)^2/\sum(\Psi_i H\Psi_i/w_i)^2$, $\langle T\rangle \equiv \langle \nabla\Psi\cdot\nabla\Psi\rangle$, H ≡ the system's Hamiltonian. Note the anomalous accuracy of H and that the estimated error, σ, does not display $1/\sqrt{N}$ convergence until $N_{eff} \approx 43$. Also, note that $\langle T\rangle = -\langle H\rangle$ and $\langle V\rangle = 2\langle H\rangle$, in accord with the virial theorem. All expectation values are in Rydbergs.

CONCLUSION

Systematic methods, such as trapezoidal, of evaluating multi-dimensional integrals have the disadvantage that they require an enormous number of points before they can adequately sample the integrand. Biased selection allows one to reduce N in exchange for using his knowledge of the integrand. For example, Hartree-Fock wave functions can be used as weight functions to find the integrals of more exact wave functions. In addition, biased selection allows one to adequately sample the important regions where the electrons approach the nucleus, or each other, closely. (These regions are important because small errors in the wave function will be amplified by the $\frac{1}{r}$ dependence of the potential. But since these regions occupy a relatively small volume, they will not be likely to be sampled. This will in turn cause the error estimate to be deceptively small.) The price paid for this flexibility is that the points must be distributed in a non-uniform manner and the correct weight function to compensate for this must be calculated. A final important aspect of biased selection is that it allows for the possibility of finding unexpectedly large values of f/w. (One technique for doing this is to uniformly and randomly sample the regions believed to unimportant, for dimensionality $\leq$ 12. For more dimensions other methods must be devised: e.g. $\psi^{2\alpha}$, where $\alpha < 1$, could be used.) These will undoubtedly ruin a good many papers which seemingly needed just slightly smaller deviations, but the discovery also enables one to find better weight functions, and eventually, to find the correct value of the integral.

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APPENDIX B
SOME c_i's WHICH FORM SOLUTIONS TO EQUATION (4) OF PART I

This appendix is a compilation of some sets of parameters, twenty-four c_i's, which form solutions to equation (4) in Part I. The headings to the sets of c_i's are laid out as follows:

22. & 1.0 G,

where $a = 22.a_B$, $r_{AB} = 1.0$, $P_{JC} = P_G$, and the lack of a "K" signifies that $\tilde{k} = 0$. If "GK" were used in place of "G" then $k = \frac{\pi}{a}$ (1, 1, 1, 1, 1, 1). Note that $r_s \simeq \frac{a}{2.03}$. The c_i's are from left to right in each row.

22 & 1.0 G

5.45253 1.71687 -1.50369 -.662024 .512976
-.272267 .218721 -.0976309 .0672783 -.0251432
-.00575232 -.0147098 -.0362 .0135635 .000883105
.0071574 -.114696 .0135826 -.00841247 .00372044
.00657276 1.28104 .0469787 .000189845

22 & 1.4 G

3.89767 2.48038 -1.16991 -.87532 .49554
-.426513 .258449 -.112614 .0324457 -.0232371
-.0465648 .0667345 .00111768 .0185579 .0293377
.00739149 .00431471 -.000247546 -.0151876 .0123873
.00679808 1.62693 -.188704 .067456

22 & 2.5 G

2.44178 2.80047 -1.07003 -.97485 .476162
-.0734526 .203358 -.0317995 .00633546 -.00699876
-.00995919 .0264261 .0122042 .00133731 -.00175191
.00831653 -.00496228 .0008735E -.00771743 .00357605
.00379001 .455529 .0636454 -.0351453

22 & 5. G

.86484 2.68932 -1.35956 -1.51112 .551501
.608982 .108947 -.895791 .51926 -.239661
-1.82782 1.12354 .482346 .13721 .108638
.0467131 -.000768374 .00751892 -.0126627 .0142958
.269243 .569531 .293583 -.243716

22 & 1. E

9.79604 2.41877 -.221294 -2.24931 2.5539
-.00294875 .472025 .0567871 .228159 .259165
.0290706 -.0626061 -.0655341 .00257433 -.00965766
-.00116609 -.666173 .0281946 -.0175874 .0128155
.0123794 1.45267 .0114822 -.0443525

22 & 1.4 E

6.51765 2.47922 .196927 -1.08067 1.29268
-.691783 .50457 .250655 .108656 .169826
-.180081 .244985 .0870172 .0104181 .0511503
.00527028 .00923478 .00193199 -.0073204 .00610576
.0420515 5.80021 -.203152 -.0199868

22 & 2.5 E

-2.26643 1.25281 -.0935228 1.57406 -2.559859
-3.71881 9.31001 -5.07662 3.00956 -8.17701
-1.23873 6.44849 2.80698 2.276023 1.74783
.152882 -.0417232 .0506946 -.1046281 .169794
.1048 9.99352 -.816278 .415844

22 & 5. E

-7.28642 1.90526 -1.45214 1.178 -5.51162
-1.67907 6.62043 -2.38639 3.68849 -2.50488
-.246736 4.54574 2.99831 .967757 .638429
.0408065 .0420574 .0555465 -.093742 .0566238
.247029 2.25731 1.8565 -1.25996

7 & .7 G

.808634 .367838 1.10213 .0577388 .296987
.0405503 -.09284 -.015956 -.100718 -.0153896
.0603024 -4.5581 -3.34419 -1.1032 -.788383
-1.37737 -1.81124 -.927221 5.66354 -4.45407
-7.28978 .848395 .071288 -.0384779

7 & 1.4 G

.481469 .270501 -.0183554 -.147389 .0568767
-.0210456 .0233409 .0115856 -.0267772 -.00496709
-.00168293 -.0682038 .0192743 -.0099876 -.0239055
.0119419 .0111319 -.0397716 .156139 -.133501
-.31089 1.0741 .0541095 -.0188915

7 & 2.1 G

.732829 .488502 -.00924068 -.0348024 .618622
.0151672 -.0653833 -.0407695 -.08142126 -.0941925
.00598963 -.00765814 .000380396 -.0000107138 .000217986
-.0006464 .000573316 -.00268044 .00598939 -.00419664
-.00811611 .416217 .01156929 -.00712904

7 & 4. G

.943901 .783469 -.616351 -.0475801 .206928
.0736034 -.0115854 -.257859 .0745104 -.0505936
-.114812 -.515653 -.144165 .0030647 .0463784
-.0265687 -.0129225 -.0353934 .111192 -.103978
-.374468 1.84667 .132764 -.00390177

7 & 6. G

.340903 -.0162407 -.377404 -.356173 .0556194
-.0485477 .0822796 .238177 .0986887 -.00683285
-.000131041 -.00797737 .0115565 .0297882 -.00738247
.000180389 .0774894 -.00108238 -.0258003 -.493195
-3.33652 9.89799 -.281797 .0378118

6. & .7 G

.999872 .304633 .816051 .0282304 .183647
-.0117636 -.0267538 -.0019381 -.0950404 -.0140295
.00763626 -4.07512 -3.03542 -.676836 -.331668
-1.23952 -1.56327 -.619112 5.90178 -4.6099
-5.56695 .882361 .120174 -.0316187

6. & 1. G

.993274 .336831 .0322636 -.135719 .222058
-.0278307 .0215007 -.0205931 -.0492358 -.0190133
-.00378005 -.336957 -.175089 .0811609 -.16067
.0847402 -.092241 -.160526 .48705 -.33228
-.751136 .977751 .221827 -.0192453

6. & 1.4 G

.403898 .0425998 .00223583 .000507758 .12307
.0178114 -.00533254 -.00938574 -.0375081 -.0139143
-.0196725 .00148256 -.0570619 -.000568257 -.00562378
-.0138714 -.0310901 -.093716 .243856 -.143064
-.143064 .647833 .0349968 -.0191335

6. & 2.1 G

.512238 .153144 -.00874024 -.0889581 .0744925
.0756689 -.0266956 -.00830042 -.0420707 -.0064518
.0127181 -.0216736 -.00173564 -.000060526 .0015734
-.0023727 .0012383 -.00382614 .00698454 -.00453195
-.00972202 .864395 .084437 -.000799673

6. & 2.8 G

1.15887 .499014 -.803264 -.424744 .154854
-.01589995 .116603 -.114598 .109916 -.0370554
.000694444 -.054303 -.201445 .0990926 -.00510171
.0202202 -.01376 -.0884194 .19433 -.131791
-.522136 .802187 .131343 .000880853

6. & 3.5 G

.582934 .0583701 .126138 -.0883582 .46078
.0689598 -.123313 .035809 -.161214 -.118069
.0438726 -.0180514 -.0311746 -.00205878 -.000530559
-.000714579 -.00180071 -.0001813 .010178 -.0132202
-.0434458 .908775 .0928176 .0182599

6. & 4.5 G

2.21822 .175554 -1.28856 -.382912 .339041
-.00152078 .419925 -.00197797 .0532977 -.047046
-.0194078 2.42218 -.0710333 .0435894 -.120948
-.00577958 .200234 .00930479 -.0204499 -.651289
-4.04488 4.69094 .10051 .0122861

6. & .7 GK

.608922 -.10828 .27076 .0014042 .15582
.028845 .046449 .03791 .0049973 -.0022803
-.031719 -.375984 -.950656 .06452 -.5238
-.24842 -.83974 -.0099339 2.2307 -1.6691
-1.6672 .67207 .59126 -.032787

6. & 1.4 GK

-6.25938 -6.874176 -1.53923 .463272 -1.53047
-.0204744 -1.09672 1.14409 .551053 .129076
.690799 -.116889 -.152821 -.0366009 -.0329876
-.529634 .138629 -1.92651 6.73739 -4.90517
-7.34396 4.45156 5.08985 -.513043

6. & 2.1 GK

-4.78711 -1.90765 .219767 .0979517 -.805452
.436595 -.0468216 .0608264 .450621 .13636
-.0803552 .00886701 .00151494 -.00415774 .00277261
-.00664669 .00849572 -.0268462 .0252691 -.0137084
-.0903088 .543297 .493302 .0223178

6. & 2.8 GK

-2.73789 -.230026 .13772 .345841 -.998114
-.482974 .176575 -.085419 .449929 .176539
-.0375613 -.149793 -.440619 -.0955906 -.108536
-.0479309 .0893655 -.414912 .687641 -.478835
-1.94372 7.79768 6.97091 -.133261

6. & 3.5 GK

-3.76914 -.260786 .119386 .381572 -.712763
-.637248 .212816 -.134683 .951148 .123978
-.0551912 -.163327 -.471025 -.0392437 -.147094
-.0588323 .108191 -.675043 .970255 -.736645
-3.73698 7.12777 6.94929 -.0992998

6. & 4.5 GK

-6.46281 .0321666 .554595 -.154165 -.896804
.148621 3.52096 -.141926 1.34993 -.0383212
-3.49655 -.593509 1.75482 .0163387 -.00290803
-.286738 -.015798 -.118612 .51913 .114581
4.02877 .32498 .11279 .00704361

6. & 1. E

-.359149 .386965 -.0333688 -.0595855 1.06056
.000158135 .012125 -.0755991 .0544618 -.0421097
.000914361 -.215127 -.820923 -.0165551 .0182192
-.0386458 .0150626 .222924 1.10414 -1.20168
-.872019 1.72058 .137521 -.0125466

6. & 1.4 E

.93706 .00636058 -.000633 .000702245 .229242
.0134293 -.0168112 -.0134842 -.0437538 -.0200026
-.0349277 .00198247 -.0656356 .260237E-04 -.0133587
-.00240967 -.0201225 .0156215 .177746 -.170412
-.19497 .74047 .063606 -.0112048

6. & 2.1 E

.903014 -.109996 -.0120655 -.157242 .128985
.135232 -.110649 -.00654293 -.0763787 -.0124782
.0228408 -.0368515 .000123393 -.960838E-05 .00484971
-.00322753 .00205743 -.000117265 .00563137 -.00588031
-.0294353 1.24902 .187426 -.000535453

6. & 4.5 E

1.59401 .166177 -.81365 -.369392 .341836
-.00120815 .435384 -.00206602 .0463201 -.0413104
-.0217937 2.26884 -.0727125 .0349618 -.116659
-.0044597 .115035 .00733502 -.0172796 -.474062
-3.55928 5.36284 .13304 .0124572

6. & 1. EK

-1.02382 .312499 .00583193 -.0826135 .828956
-.0176545 .0287117 -.0974467 .0403062 -.00233446
-.000946246 -.0266974 -.859021 .00579986 -.355382
.0170031 -.00373963 -.157419 .918115 -.734089
-.605029 .465367 .338817 -.00100792

6. & 1.4 EK

4.14915 -.122743 .0180227 .00130893 .6658013
.201956 -.0483587 -.0248006 -.289425 -.0850231
-.0588636 -.00335191 .443182 -.000178247 -.066419
-.0797879 -.161631 -.737539 .0721878 -.0710252
-2.21844 1.01373 .346956 -.0453018

5. & .7 G

1.05627 .259298 .741654 .0139225 .330218
.00436738 -.0348232 -.00674219 -.127492 -.0226627
-.00398958 -7.3068 -2.30689 -1.6895 -.339471
-.762712 -1.17604 -.720449 5.53218 -5.2129
-10.9573 .910643 .233424 -.0142728

5. & 1.4 G

.351895 .266686 -.111607 -.095252 .0572138
-.0649698 .0235298 -.0127587 .00211684 -.00811348
-.000553647 .036532 -.119704 .0289219 -.0426376
.0316559 .00729109 -.0768738 .191986 -.123062
-.241364 .638106 .138458 -.00475326

5. & 2.8 G

1.01928 .509863 -.781018 -.298329 .272656
.0690349 -.0914176 -.0753137 .123082 -.07433555
-.0722998 -.311707 -.342193 .125316 .00954091
.0943528 -.0196233 -.156103 .171616 -.0793897
-.19793 .759801 .0901513 .0101635

5. & 4. G

.890985 -.0419985 -.642047 -1.04209 .204482
.035678 .484857 -.366288 .0100374 -.0910031
-.222302 1.69693 .430792 .119823 .677723
.0191797 .315474 -.0385253 -.176957 -2.33009
-9.85889 1.85168 -.0119261 .05767

5. & .7 GK

-.880133 -.00834626 -.0207695 -.000597221 -.0222559
-.000276672 .00209088 .000320698 .00786145 .000712109
.83542E-04 .262764 .147525 .1242908 .047284
-.0128878 .0900391 .0699751 -.361025 .318289
.716716 1.22457 .462269 -.0191604

5. & 1.4 GK

-1.206 -.336949 -.0121661 -.0932783 -.0132759
.100572 .019481 -.0504815 .00580886 .000614979
.829535E-04 -.0614424 -.658208 0490576 -.725265
-.0012495 -.01815 -.496898 1.40316 -.909643
-1.60067 1.71658 1.7921 -.025796

5. & 2.1 GK

8.21846 -.225419 -.563867 .365504 -.338896
.0219977 -.273293 .00517749 -.698519 .376634
.232002 -.160929 -.000593355 -.000453646 .00212904
-.000192353 .00172613 .00679883 -.0076754 -.00240923
-.0277538 4.18932 1.42478 .000654507

5. & 4. GK

.537897 -.00730111 -.283427 -.0222135 .202403
.00208664 .385397 .0297808 .0135025 -.0109746
-.174762 .357908 .417361 .0422085 .779853
.00762719 .059207 -.00106257 -.0123419 -.557983
-2.86379 1.88094 -.0177811 .0447337

4. & .7 G

-1.34137 -.0295193 .0719105 .0243236 .00036063
-.0498882 .00474802 -.00101707 .00472456 -.000190988
.0108448 2.26266 .0347953 -.5594155 -.735385
.800162 -.588527 -.46292 -.00518431 1.0059
2.3849 2.01827 .248512 -.00210663

4. & 1. G

-.477832 -.0200384 .155021 .0580049 -.00261883
-.0201761 .000688027 .00518321 -.00666811 -.200719E-04
-.0109771 -3.43527 -1.31028 -.0977203 -.312343
-.00389155 -.785948 -.045683 -.675351 .125076
-7.9765 6.14652 1.16283 -.0334169

4. & 1.4 G

-.464054 .0167439 .217454 -.00467966 -.0492232
-.110493 .0280303 .0430283 -.0227969 .0079566
.00195698 -3.60013 -1.42279 -.19831 -.449941
-.14783 -.922565 -.180047 -.808834 -.00775902
-7.94649 1. -1. .00001

4. & 1.75 G

1.58386 -.257572 -.414904 -.668333 .199658
.200211 -.123333 .0435489 -.0554079 -.0293466
.244442 .0857579 1.45333 -.34844 -.080133
-.0158724 .0959436 -.0534119 .553248 -.712648
-1.4507 1.97703 .249875 .00709993

4. & 2.25 G

1.47644 -.395068 -.546909 -.647157 .18311
-.0164863 -.0724931 -.21139 -.00561677 -.0137878
.436996 .138887 1.51684 -.342682 -.112284
-.0575647 .0545064 -.0973971 .506628 -.761794
-1.38135 1.98364 .194017 .023575

4. & 2.8 G

1.43478 -.443678 -.574064 -.626681 .0990152
-.0690079 -.0450037 -.275788 .000362674 .0216476
.497174 .149369 1.56209 -.31789 -.105251
-.0479535 .0674437 -.0833989 .519053 -.747503
-1.39776 1.99109 .0637323 .00651043

4. & 3.45 G

-1.51982 -.138012 .622281 .4611906 -.115573
-.248374 -.162853 .197609 -.0873137 .0710092
.229392 -.986832 -.10661 -.102881 -.128541
.034485 .0357477 -.124313 .00225508 .291915
.795946 .847298 -.00740728 .00568203

4. & .7 GK

-1.2186 -.106932 .0668585 .0273917 -.106244
.02666661 .0115813 -.0533193 .0167068 .0104495
.00147221 4.20263 .062649 .979817 .330732
-1.67531 -.0255937 -.136045 .000998754 1.2519
6.51349 .535701 .488841 .017845

4. & 1. GK

-1.11692 -.15621 .0870161 .0351861 -.106294
.033635 .0211912 -.0746079 .0325898 .00874146
.0020378 5.82896 .0765675 1.4472 .53707
-2.3423 -.0303509 -.167822 .00114746 1.70953
9.36861 .509093 .481717 .0097323

4. & 1.4 GK

-.9191 -.134083 .0755982 .0310222 -.0646937
.0354289 .0120291 -.07138 .0379446 .00735838
.00218033 5.67214 .0544314 1.28115 .457757
-1.16516 -.0297432 -.12915 .00113571 1.52498
9.78121 .729631 .657794 .0338287

4. & 1.75 GK

1.19517 .443559 -.0330208 -.163753 .356383
-.107767 .0418882 -.0453108 -.162186 -.0752388
-.000836007 .514238 .045803 .000550776 .1271
-.000160524 .00172179 -.0400537 -.127488 .29822
1.34006 2.13725 2.18828 .0565107

4. & 2.25 GK

-.476618 .0100676 .0700191 .00384932 -.0551631
.00203574 -.0263839 -.0260537 .0832772 .00706662
.0180382 .00232655 .515817 -.0137673 .0606093
-.000817234 .601903E-04 .0022957 -.0227172 .192549
1. 4.13941 3.49584 .0368447

4. & 2.8 GK

1.3005 -.00064607 -.234954 -.0162649 -.00198002
-.0165385 .197211 .0520056 -.24861 -.0174046
-.0297964 -.0765833 -4.06888 .0363056 .279387
-.0239216 .000986673 -.00932823 .136613 -.525247
2.0173 4.95212 2.45454 .0670788

4. & 3.45 GK

-1.44876 -.119917 .808179 .462445 -.271526
-.476972 -.27387 .354734 -.181314 .0271339
.318395 -.31205 -.0861472 -.106382 -.324276
.0450396 .0217349 -.183637 .00201017 .273574
1.21442 .8963 -.0133977 .00613955

4. & .7 E

-1. -.000466451 -.00520523 .0220344 .411652E-04
.00274884 .000340835 -.000190829 -.000147843 -.379363E-04
-.00308894 1. .147 -.132456 -2.71289
-2.87831 -2.5419 -.763603 -.0205172 3.30906
6.88461 -1.19465 .158041 .00117802

4. & 1.4 E

-1.04954 .0738691 -.0298693 .0540486 .000225375
.000493738 .251657E-04 -.012523 .00715604 -.000457317
.00246386 .498456 .0316727 -.142918 .14203
-.287652 -.0397597 .00340031 -.192288 -.000889265
-4.33326 7.73088 .00237376 .0610444

4. & 1.75 E

6.02688 -.890945 .00939682 -.404658 -.0134625
-.0184903 -.00606713 .0212773 -.232104E-04 .0343392
-.031069 -.0401281 -.699684 .0468645 -.115585
-.0179792 -.00249136 .157443 .0342816 -.000359447
-1.05119 3.93394 .108828 .000356914

4. & 2.25 E

-7.85916 -.432213 -.607039 .977644 -1.06654
-.531162 -.209371 .395779 .167058 .376396
.0269044 -.43156 -.338204 -.295362 .194229
.0248839 .166162 -1.31903 .0115401 .75117
.666527 7.15127 .059679 -.0183839

4. & 2.8 E

.508639 -.0982552 .0222123 -.05494557 -.000429258
-.00193939 -.0409094 .0768409 .112198E-04 .0011388
.00372063 -.0218034 .15694 -.00344455 .0890267
-.0173317 .0161659 .0601164 .113709 -.198512
-.716933 2.41848 .00771705 .00105531

4. & 3.45 E

-8.71381 -.769017 -1.27287 .975751 -1.23709
.331149 -.302317 .537242 .130226 .182246
.0201789 -.690498 -.431524 -.141376 .362753
.310502 .0679545 -1.40271 .0308805 .860379
1.05234 5.67635 .0324755 -.00953438

3. & .8 G

4.54957 -.0469112 .00671884 -.229976 .00102684
-.088406 -.0208195 .392524 -.187449 .0304469
.00648935 -2.31205 .426022 -.224352 -.707107
-.138508 .328661 1.92961 .7683393 -3.02612
-4.06172 2.03149 .104738 -.000636008

3. & 1. G

7.31958 3.07411 -.94805 -.63843 1.51335
-.658162 -.664636 -.046448 -.450327 -.1689636
.145493 -3.87345 -.0145691 -.871474 .466132
-.518968 .110714 .167214 -.576905 .0338673
-1.15158 4.67594 .291272 .00479672

3. & 1.2 G

7.37126 3.09256 -1.00765 -.651031 1.12144
-.64434 -.716007 -.0747696 -.53826 -.155878
-.0474769 -4.69158 .0255857 -.575091 .150096
-.169435 .374616 .297299 -.535184 .0813895
-.565104 4.62951 .690035 .0324559

3. & 1.4 G

3.18182 -.000174876 -.000932949 .000902208 .634194
-.000625446 .000274685 .00243311 -.000726496 -.00630803
.000512782 1.65 -1.26702 .00266873 .0452624
.115553 .0110213 .292955 .347149 -.939683
-1.01366 .593841 .059868 .00740655

3. & 1.7 G

3.18153 .000600124 -.000697516 .000982334 .6357
-.327607E-04 .000380024 .00385713 .00161169 -.000275974
.000620208 1.65198 -1.26789 -.000601359 .0410849
.111049 .00658103 .288834 .343489 -.942622
-1.01067 .59647 .00316225 .000365323

3. & 1.95 G

-.69359 .165429 .218206 .0579716 -.0980123
-.0661584 .107275 .117531 .0404155 .00323545
.0187104 .389407 -3.22243 -.357248 2.66393
2.17258 -.336104 .238991 .901465 -3.64053
-6.0388 7.14031 .485594 .114841

3. & 2.2 G

.25574 .00794733 -.000105811 .0114902 .0316643
-.0020656 .00183107 .0055899 -.000157365 .0454615
-.0078063 -24.2644 -.493401 -.0255167 -1.09244
.0680123 .0261596 .00529 .565882 -.751697
-1.06419 2.33024 .00167776 -.000686044

3. & 2.55 G

-.525264 .237914 .196799 -.0753164 .00124258
-.334862 .00186811 -.0223282 .0235775 .173906E-04
.0408157 .50025 -2.79318 .00918744 2.99448
2.38024 -.278783 .265502 .884892 -3.69059
-5.9718 7.15326 .114133 .0478415

3. & .8 GK

5.377 -.00235305 .0169123 -.0688899 .125064
.449175 .00326769 -.000917241 .0294095 .00177857
.0122926 2.18648 -.268457 .0205866 -.0285267
-.122373 .0490895 .171355 -.000132097 -.196505
-.339374 -1.05071 -1.05027 .000392251

3. & 1. GK

1.37916 .00126133 .0128358 -.175917 -.0229163
.0563418 .000513313 -.058718 .00633293 .00167228
-.0106791 2.50361 .0470755 .106002 -.200307
-.0177135 .0391481 .0249471 -.00594399 -.0392893
-.09606 -.669114 -.744293 .711075E-04

3. & 1.2 GK

1.71265 .000816346 .0103548 -.156562 -.011778
.0734655 -.196004E-04 -.0933257 .00199497 .00179311
-.0100391 3.5082 .0718827 .0112093 -.0389181
-.0135897 .00674364 .0430364 -.00941467 -.0477697
-.113945 -.740692 -.861249 .786136E-04

3. & 1.4 GK

1.87963 .00018834 .0144051 -.136636 -.0295948
.0531575 -.347293E-04 -.076596 .00135121 .00299131
-.00837353 3.82941 .0570866 .0506361 .00737841
-.0121464 .0279308 .0332995 -.0105837 -.0613134
-.13864 -1.01433 -1.090294 .000118932

3. & 1.75 GK

.304446 -.00165579 -.131914 .000248318 -.00120863
.000159425 .000679926 .771264E-06 -.000349501 .158105E-04
.153452E-04 .176164 .00208872 -.000411351 -.924127
-.00207401 -.936073E-04 .317731E-06 -.204651 -.539558
-3.03406 3.41088 2.99772 .0350205

3. & 2.2 GK

.583401 -.00309683 -.21684 .000378205 -.00270008
.000540415 .00580322 .8170554-06 -.00112048 .784774E-04
.500787E-04 .421803 .00880374 -.00203501 -1.05312
-.0101896 -.00355381 .3750441E-06 -.301038 -1.04555
-4.51092 7.21316 2.48423 .104707

3. & 2.55 GK

2.1785 -.00432416 -.974641 -.000237863 .000471424
-.000303637 -.0529644 .721503E-05 .00197343 .000177692
-.286876E-05 1.2237 .0448264 -.000689399 -.160338
.0535872 .0031392 -.29754E-05 1.25398 -5.86435
-6.09737 -1.12854 -6.34452 .202719

3. & .8 E

-9.85374 .0903145 .425609 -1.35953 -.566749
-.0017652 -.0775017 -.0448593 .0152553 -.233186
.457196 -1.00992 -.84681 -.043007 .137123
.0233746 .00923187 -.062861 -.0585851 -.0653404
-.253065 6.9881 .590429 .00959872

3. & 1.3 E

.248764 -.0121822 .00157445 -.0116369 .101762
-.010368 -.664804E-04 .000632329 -.000513666 -.0656477
-.00110905 -.0526031 -.00286657 .0175151 -.0259384
.0290269 .000900645 .049882 .0360132 -.0309902
-.445575 .952933 .0588593 .000558181

3. & 1.5 E

1.65403 -.0424279 -.00708947 -.236553 .429861
-.062289 .0350777 -.00907606 -.0565782 -.233732
.0369542 -.704132 .388013 -.422118 -.500828
.0289222 -.0179963 .179528 .0584634 -.049494
-1.5994 4.00686 .130799 -.0226223

3. & 1.7 E

1.03664 -.019329 .0520827 -.0929843 .331554
-.0180385 .0166849 -.01544642 .00792924 -.116472
.0761892 2.51748 -.0226852 -.0771914 -.0318474
.684615 -.0068679 .2072 .430328 -.741016
-1.4782 5.93666 .170697 -.0197655

3. & 2.2 E

-.605918 .259495 -.0183721 -.0391696 .00302436
-.0797304 .00244577 -.0304951 -.0391204 -.433413E-04
.027905 -.730746 -.189141 -.0186869 2.48587
.365944 -.11239 .125445 1.10173 -1.72249
-3.89127 8.13134 .222414 .0315895

3. & 2.55 E

-1.14117 .927488 -.00374476 .121085 .00484935
-.328316 .010948 -.0691217 -.100349 -.000372127
.184447 -1.37797 -.215946 -.0219576 3.06324
-.0328806 .0480139 .306817 1.74555 -1.97162
-5.31645 7.57 .148788 .0336732

3. & .8 EK

-9.00884 .0104799 .0283241 -.263324 -.0676639
-.001448 .0167284 -.167606 -.508565 .0296039
-.000528373 -.525359 -.977103 -.0703406 -.0955005
.150209 .23801 -.0664694 -.21159 -.172021
-.572865 7.17687 8.77046 -.0355244

3. & 1. EK

-3.88426 .872749 .236505 -1.15792 1.19953
-.444463 -.161751 -.0189474 -1.45377 -.234358
.095499 -9.45776 1.11258 .253461 .735305
.123893 .0142571 -.121973 -.889028 .00592028
-1.15349 9.20664 1.59249 .00247565

3. & 1.7 EK

.438773 -.0015238 -.00507751 -.000509462 -.110447
-.000636213 -.00486389 -.00411117 .000606257 .00319358
-.000268826 -1.90009 -3.191919 .02482198 1.47762
.803197 .0286416 .976997 .252868 -1.40383
-.875955 4.85769 -.00509545 .00309971

3. & 2.2 EK

-.767891 .350204 .221753 -.0637924 .00485957
-.366187 .00468834 -.0236328 -.114741 -.000165024
.0483026 -2.30821 -2.58719 .163242 2.74302
1.66928 1.556 .121151 1.37077 -2.56467
-2.49438 7.19244 .589523 .143086

2.5 & .7 G

3.12734 .343355 -.0108685 1.03941 .0130322
.00687696 -.00509265 -.0459078 -.158252 .0051976
-.309554 5.63389 .6056576 .0308444 3.30814
.0198433 -.0749837 .400315 -3.1478 .170127
-5.21059 3.11545 .199584 .00347407

2.5 & 1. G

2.31433 .354808 -.0108066 1.1705 .020443
.00947228 -.00933654 -.0502323 -.192271 .0172044
-.510483 6.45437 -2.42413 .0420169 1.76911
.0276455 -.0768791 .46458 -1.94692 .1656
-2.71905 2.28952 .13177 .0034102

2.5 & 1.2 G

1.92097 .319094 .00712546 .638403 .0856298
-.106647 -.148625 .0346882 -.232141 .00210723
-.217264 6.211991 -2.14314 -.0539591 3.70569
-.21453 -.0314688 .370219 -2.3796 .0876014
-3.5945 2.14221 .125532 .00362669

2.5 & 1.4 G

1.5743 .219832 .048025 .550603 .0841845
-.189597 -.0968006 .0204073 -.289116 .0204817
-.320556 7.96244 -3.26056 -.139658 2.63659
-.140643 -.0023666 .188339 -1.30422 .0807703
-1.3336 1.7692 .0709753 -.000227715

2.5 & 1.75 G

1.90362 -.126961 -.246556 -1.80271 -.00187333
.467704 -.377433 .0623958 -.34587 .0372722
1.20556 -1.73606 .89766 .80353 -.139786
.39685 .0243075 .419039 -1.06141 .117238
-.745717 .939662 .000413687 .0031294

2.5 & 2. G

.880396 -.110341 -.193692 -.713726 .0268201
.371339 -.378624 -.0133993 -.237087 .00197466
.569392 -.0243136 -1.15414 .600598 -.361546
.503315 .00591096 .515512 -.985635 .216452
-.376334 1. 0. 0.

2.5 & 2.15 G

.732913 -.14596 -.175345 -.586525 .0288397
.294305 -.263993 -.00949506 -.184851 .00169938
.564126 -.0151023 -1.44465 .636112 -.451972
.487061 .0060675 .518624 -.857519 .173248
-.291257 .883707 .00100188 .00094576

2.5 & .7 GK

1.69269 .247301 -.307191 .323369 -.00821718
.00564997 -.0283394 -.00550127 .00230643 .773192E-04
-.0777091 5.580711 .139181 -.182641 .87069
.435138 -.000527842 .425563 -1.42891 -.0565672
-4.30958 1.57651 1.77402 .000300383

2.5 & 1. GK

1.85835 .282381 -.509886 .436532 -.0118781
.0112552 -.0522782 -.00477234 .000948503 -.000375387
-.141246 4.85359 -.192472 -.462647 .831682
.484277 -.00306192 1.33921 -1.93034 -.0329698
-3.45824 .590357 .636394 .000111688

2.5 & 1.25 GK

1.89625 .0433578 .0181619 -.049779 -.00826405
.000454365 -.0767548 .00151659 -.26323 .00945894
-.0450634 .335803 2.93495 -.631096 .618001
-.0585302 -.00175778 .892575 -.981799 .0363607
-.777745 .67315 .537619 .0105408

2.5 & 1.4 GK

2.27823 .125413 -.136463 -1.28001 .11676
.228794 .0188651 -.0195081 -.231865 .00440673
.552801 -6.14832 -.305329 .071227 .0549223
.259433 -.00925621 -.0929985 -.325338 -.497594
-2.362875 1.5979 1.58745 .0222886

2.5 & 1.75 GK

2.75524 .00290017 .00116782 -.098551 -.000738376
-.000179532 .0073079 .00229662 -.530769 -.00113228
-.0115516 .80643 .677491 -.0224857 3.114214
-.0047878 -.000110941 -.398021 -2.07068 .0389272
-4.27666 2.19704 1.39469 .030199

2.5 & 2.15 GK

-.370562 -.00222894 .000673023 .0128396 .53239E-04
.000117607 -.000483836 -.00097996 .129331 .000166927
.00326745 -.160764 -.0294859 .0228699 -.506646
.000315916 -.179892E-05 .0612475 .818405 -.0138183
1.19826 .308589 5.54238 -.00452686

2.5 & 1. E

5.1194 -.0385783 .0700439 -.328775 -.0290115
-.259048 .375664 .169508 -.033565 .017309
.247376 3.48253 -6.79051 1.40641 -1.17974
-.335617 -.165585 2.5251 -1.6516 .261532
-.942128 1.17803 .0583131 -.00326765

2.5 & 1.1 E

5.12517 -.213843 .0311153 -.319889 -.0139709
-.301488 .371758 .198875 -.0596792 -.0325276
.209978 4.34689 -6.15337 .843351 -1.12143
-.0680962 -.0970094 2.67285 -1.6605 .00231656
-.826448 1.17927 .017953 -.00372299

2.5 & 1.2 E

3.07485 .332756 .204362 .175381 -.327187
-.551466 .743215 .124694 .320149 .0729359
.109272 3.86797 -10.3012 -.497307 5.09774
.0434727 -.036299 2.78676 -2.59686 -.125148
-.953589 .850428 -.0232027 .00247386

2.5 & 1.4 E

1.24877 -.168445 .141241 .332148 .0188992
-.523681 .0914282 .0433416 -.450358 -.0390543
.0573283 1.69369 -1.32811 -.120077 4.09392
-1.07639 -.0580292 2.34624 -3.26934 .447635
-2.00775 2.20387 .0789998 -.0149201

2.5 & 1.75 E

9.30867 -.597198 .187005 -1.87098 .0422725
.108313 .28365 .236104 .464553 -.20278
.0805101 -2.14811 -.104295 1.01489 -2.24482
-.261669 -.126258 7.5701 -5.24055 .150421
-1.20365 1.5141 .0690978 -.00250879

2.5 & 2.15 E

3.92124 -.968814 .0760087 -.796784 .0287254
.172552 .426077 .232567 .376058 .0606417
.121489 -1.94693 -1.25445 .411459 -1.72555
-.243261 .611487 4.01324 -3.52209 .509019
-.76868 4.18482 .059053 -.0587498

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BIOGRAPHICAL SKETCH

Stephen A. Burdick was born in San Antonio, Texas, on July 27, 1952. He attended and completed his undergraduate work at the Georgia Institute of Technology on a tennis scholarship. After receiving his B.S. degree from Georgia Tech, he continued his studies at the University of Florida, from which he received his Ph.D. in December 1980. He and his wife, Linda, have one daughter, Leslie.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Arthur A. Broyles, Chairman
Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

F. Eugene Dunnam
Professor of Physics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Astronomy

This dissertation was submitted to the Graduate Faculty of the Department of Physics in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1980

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and Research